

**Chromium Speciation Monitoring Platform for Drinking
Water: Machine Learning Assisted Dual-Emission
Fluorescence Sensor Array**

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ABSTRACT

Different chromium (Cr) speciation in drinking waters shows distinct risk levels to humans, failing to reflect real environmental impacts only by total Cr analysis. Although instrumental methods can accurately distinguish Cr speciation, complex pretreatment processes result in a low detection efficiency, making it impossible to achieve rapid and on-site analysis. To solve this problem, integrating with machine learning, a novel fluorescence sensor array was developed for rapid identification and quantitative detection of Cr speciation in waters without sample pretreatment other than filtration. This system prepared a three-component fluorescence hybrid material (MSN@Zr@Au and MSN@Zr@AgAu) with dual-emitting wavelengths. Benefiting from these probes, this sensing unit was specific for Cr speciation and accurately identified different chromium among eleven coexisting cations. A dual-mode algorithm could effectively improve analysis accuracy. The algorithm of linear discriminant analysis (LDA) assisting hierarchical cluster analysis (HCA) provided higher selectivity to Cr speciation for both single-component and mixed real samples. Finally, this sensor array showed good analytical performance in a linear range of 1-60 μM , exhibiting a low detection limit of 1.29 μM . This dual-emission fluorescence sensor array shows excellent practicability for Cr speciation analysis in drinking and tap water, which is expected to develop a practical monitoring platform for real water.

KEYWORDS: Rapid detection, fluorescence sensor array, chromium speciation analysis, environmental waters

SYNOPSIS: This study highlighted the potential for developing a machine learning-

assisted dual-emission fluorescence sensor array to rapidly distinguish chromium speciation without sample pretreatment other than filtration, providing a feasible alternative for controlling chromium pollution in drinking water.

■ INTRODUCTION

Chromium (Cr) pollution in environmental water is a typical problem that has been widely discussed.^{1–3} Chromium element exhibits various valence states, and its oxidation states cause different levels of harm to groundwater.⁴ Whether it's Cr (III) or Cr (VI), both of them are harmful to animals and plants when entering the environment.^{5–8} Thus, it is necessary to develop novel methods to identify chromium speciation in groundwater. Currently, instrumental methods are primary analytical techniques.^{9–11} However, it is limited owing to high pre-processing requirements, long detection time, and relatively high cost. Recently, fluorescence methods have been widely applied to detect environmental pollutants using fluorescence probes.^{12–14} These methods can achieve high sensitivity and stable signals, but most of them have difficulty in distinguishing chromium speciation. Thus, it remains a challenge to achieve simultaneous analysis of chromium speciation using fluorescence methods while keeping a simple procedure.

With the development of machine learning, machine learning-assisted fluorescence methods have shown great potential in multiple targets with high structural similarity, especially hierarchical cluster analysis (HCA) and linear discriminant analysis (LDA). HCA algorithm divides samples into multiple clusters according to similarity criteria.¹⁵ It is an unsupervised learning algorithm because data labels are not

available during learning process. PCA is an unsupervised learning algorithm like HCA, which aims to map high-dimensional data into a low-dimensional space. However, PCA ignores any additional information about samples (e.g., categories or labels) to evaluate datasets rather than for prediction.^{16,17} LDA is a supervised learning algorithm that enhances feature performance by maximizing between-class variance and minimizing within-class variance, which directly analyzes category distinction to deal with data classification and prediction.^{18,19}

Based on machine learning algorithms, the concentration matrix can be correlated with signal outputs to reduce the analysis complexity of Cr speciation in real environmental waters.^{20,21} Lu et al.²² used a combination of PCA and LDA to identify and quantify Cr(III) in a multi-component sample. Orouji et al.²³ developed a colorimetric sensor array with Au@Ag nanorods to identify Cr(III) and Cr(VI), quantifying a single-component chromium species. On this basis, we designed a strategy to simultaneously realize speciation classification and multicomponent quantitative analysis with a lower detection limit.

Integrating with machine learning discrimination, a novel dual-emission fluorescence sensor array based on zirconium-based fluorescence metal-organic frameworks (Zr-LMOF) and gold nanoclusters (Au NCs) was developed for Cr speciation analysis in drinking water. Amino-functionalized mesoporous silica microspheres (MSN-NH₂) were used as carriers to support Zr-MOF and Au NCs uniformly. Self-calibration using Zr-LMOF as reference signals can effectively improve signal stability and accuracy. In this sensor array, a database of in-cluster

89 aggregation and inter-cluster dispersion of Cr^{3+} , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ was established.
90 Under the best conditions, HCA and LDA analysis could effectively distinguish
91 different chromium speciation, showing good sensitivity, selectivity, and anti-
92 interference for real water samples.

93 ■ MATERIALS AND METHODS

94 **Preparation of MSN@Zr@Au and MSN@Zr@AgAu.** The preparation of MSN-
95 NH_2 , GSH-Au NCs, GSH-AgAu NCs, and Zr-LMOF was provided in Supporting
96 Information. In detail, 3 mL of MSN@Zr-LMOF solution was mixed with 3 mL of
97 GSH-Au NCs and GSH-AgAu NCs, respectively. The mixture was stirred for 30 min
98 and centrifuged with deionized water (9000 rpm, 5 min). Finally, the precipitate was
99 redissolved in deionized water for further use.

100 **Sensor array for Cr discrimination.** The 100 μL of different Cr speciation (Cr^{3+} ,
101 CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$) were introduced into 20 μL of probes, including MSN@Zr@Au
102 and MSN@Zr@AgAu. Five minutes later, the fluorescence intensity was recorded at
103 410 nm, 630 nm, and 740 nm under 375 nm emission excitation, respectively. This
104 process was repeated five times for 3 kinds of Cr speciation and then generated a set
105 of 2 channels $\times$ 3 Cr $\times$ 5 repetitions of training data matrix. Meanwhile, the raw data
106 were normalized by F_{630}/F_{410} or F_{740}/F_{410} , where F_{630} and F_{740} represent Au NCs
107 fluorescence intensity, and the F_{410} represents Zr-LMOF fluorescence intensity. All
108 data matrices were processed by Statistical Product and Service Solutions (SPSS), and
109 results were obtained by LDA and HCA.

110 ■ RESULTS AND DISCUSSION

The preparation of dual-emission fluorescence probes is illustrated in **Scheme 1A**. The transmission electron microscope (TEM) and scanning electron microscope (SEM) images (**Figure S1 and S2**) showed the successful synthesis of MSN, while Zr-LMOF was attached to microsphere surface via amino groups. The high-resolution transmission electron microscope (HRTEM) in **Figure 1A-1B** showed that Au element was mainly distributed in Zr-LMOF interior and MSN surface, induced by the strong affinity of Au NCs to amino groups.^{24,25} As illustrated in **Figure 1C**, with the gradual modification of probes, the characteristic peaks of Zr and Au appeared near 185 eV and 88 eV, respectively. As shown in **Figure S5-S8**, a new peak at 288.78 eV belonged to the O-C=O after introducing 1,2,4,5-Tetrakis (4-carboxyphenyl) benzene (H₄TCPB).²⁶ Meanwhile, the peak area of -NSiO₂ at 402.72 eV was greatly reduced with the C-O peak in O 1s spectrum at 531.53 eV, indicating that Zr-LMOF was combined with MSN-NH₂ by the Zr⁴⁺ anchoring to -NH₂. In Zr 3d spectrum, the characteristic peak of Zr-silicon appeared at 183.10 eV, proving that Zr-LMOF was indeed successfully bound to MSN. Seen from **Figure 1D-1E**, binding energies of Au 4f_{5/2} and Au 4f_{7/2} were located at 88.60 eV and 85.00 eV, respectively. The Au 4f_{7/2} peak could be deconvoluted to Au(0) (84.70 eV) and Au(I) (85.40 eV), and Au 4f_{5/2} peak was deconvoluted similarly.^{27,28} Thus, Au valence states in these probes were predominantly zerovalent and monovalent, as well as the main fluorescence source for GSH-capped Au NCs. The Fourier transform infrared (FTIR) analysis (**Figure 1F**) showed that the band at 3400 cm⁻¹ was assigned to N-H vibration from amino groups of 3-aminopropyltriethoxysilane. The band of MSN-NH₂

at 1630 cm^{-1} was assigned to the tensile vibration of amino groups.²⁹ The vibrational band at 1600 cm^{-1} and 1450 cm^{-1} is assignable to benzene rings of H_4TCPB ^{30,31}, and a strong absorption peak of carboxyl groups appeared at 1660 cm^{-1} . Additionally, a band around 715 cm^{-1} possibly belonged to C-H out-of-plane bending vibration of benzoic acid. Furthermore, the characteristic peaks of LMOF in X-ray Diffraction (XRD) were found at 5.3° and 8.8° (**Figure 1G**).^{14,26,32} These results illustrated that fluorescence probes were successfully prepared.

Initially, the optical performance of LMOF and Au NCs was studied in **Figure S9**. As displayed in **Figure 2B-2C**, optimal emission wavelengths of fluorescence probes under 375 nm excitation were 410 nm, 630 nm, and 740 nm, respectively. A shift from 400 nm to 410 nm appeared due to non-radiative de-excitation effect. When Zr-LMOF was excited for electron leaps, the collision with Au NCs resulted in a loss of energy. The result was also supported by a spectral redshift due to a decrease in the fluorescence frequency and energy. Different Cr speciation (Cr^{3+} , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$) and 11 other cations (Li^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Mn^{2+} , Pb^{2+} , Cd^{2+} , Al^{3+} , Ga^{3+} , and Ce^{3+} at a concentration of 1 mM) were introduced into this system. As displayed in curves, CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ completely quenched the probe fluorescence, and MSN@Zr@Au showed a more sensitive response to Cr^{3+} than MSN@Zr@AgAu . As displayed in **Figure S10 and S11**, fluorescence quenching was gradually significant as different Cr (VI) concentrations increased. However, the fluorescence response to Cr (III) is weaker than that of Cr (VI). After fitting, it was found that a good linear relationship was established between fluorescence ratio and Cr speciation at low concentrations

(0-60 μ M).

Possible mechanism between fluorescence probes and Cr speciation was studied in **Figure 2**. Fluorescence response was attributed to the synergistic effect of LMOF and Au NCs (**Figure 2A**). Firstly, three emission peaks of these probes had no obvious overlap with the UV absorption of Cr speciation, and there was no fluorescence resonance energy transfer (FRET) occurring. As shown in **Figure S4B**, a large overlap between excitation wavelength and absorption spectrum of Cr (VI) was observed, and LMOF fluorescence was quenched due to the competitive absorption of excitation spectra between the target and probe. This fluorescence quenching related to target concentrations is known as internal filtration effect (IFE),³³ which is the main reason for fluorescence quenching by Cr (VI) at 410 nm. Further considering fluorescence quenching by charge transfer between host and guest, fluorescence lifetimes were detected before and after reacting with targets (**Figure 2D-2E and Section S7, S8**). It was obvious that decay rates of fluorescence lifetimes were accelerated to varying degrees after adding targets.^{34,35} After computing by Stern-Volmer equation, it was concluded that dynamic quenching of Cr speciation to probes induced a decrease in fluorescence intensity.¹³ Dynamic mechanism analysis at different emissions was shown in **Figure S12-S14**, and K_{sv} and K_q values were shown in **Table S1**.

The decrease in fluorescence lifetime was also related to the strong oxidation of chromate. The Au NCs fluorescence was mainly from Au(I) and Au(0) reduced by GSH, and valence state change could cause the fluorescence quenching. Therefore,

XPS analysis was further performed to study the reaction between fluorescence probes and Cr speciation (**Figure S15-S20**). The Au 4f deconvolution in MSN@Zr@Au was displayed in **Figure S15F** after reacting with Cr^{3+} . At Au 4f_{7/2} orbital, Au(0) accounted for 65.6% while Au(I) made up 34.4%. The deconvolution of Au(0) and Au(I) at Au 4f_{5/2} orbital accounted for 72.6% and 27.4%, which showed no obvious change compared to that in the single probe (**Figure 1D**). When CrO_4^{2-} was present (**Figure 2F**), the deconvolution proportion of Au(0) in Au 4f_{7/2} and Au 4f_{5/2} increased to 71.2% and 77.1%. The corresponding Au(I) decreased to 28.8% and 22.9%, respectively, indicating that Au(I) was oxidized to Au(III).³⁶ With the addition of $\text{Cr}_2\text{O}_7^{2-}$ (**Figure 2G**), the deconvolution proportion of Au(0) and Au(I) at Au 4f_{7/2} and Au 4f_{5/2} orbitals increased again to 67.3%: 32.7% and 64.7%: 35.3% due to the higher oxidation, suggesting that Au oxidation in two valence states occurred. The corresponding high-resolution spectra of Au 4f in MSN@Zr@AgAu were consistent with the above results. Thus, the mechanism between probes and Cr speciation is mainly ascribed to the IFE of Zr-LMOF and Au oxidation in a low valence state.

Reaction conditions were optimized to achieve a better analytical performance (**Figure S21-S24 and Section S9**). Based on machine learning, we established a prediction model for classification and concentration analysis (**Figure 3A**). The corresponding HCA (**Figure 3B**) and LDA (**Figure 3C**) were invoked for category identification and concentration prediction. As shown in **Figure 3D-3D₍₃₎**, samples with a concentration of 50 μM were detected, generating four sets of fluorescence value data. These results were further processed to obtain a fingerprint and radar map.

Compared with a blank sample, fluorescence ratios of Cr (III) and Cr (VI) were significantly different, and the concrete classification distribution failed to be obtained intuitively. After optimization by HCA and LDA, twenty points from four data groups were accurately classified into 4 classes, being consistent with actual sample classification and achieving a 100% rate in classification accuracy. Satisfactory results were also achieved with the concentration of 10 μM and 1 μM (**Figure 3E-3F₍₃₎**).

Another advantage of combining LDA with HCA is that the score map of LDA can be applied for quantitative analysis in this sensor array. The highest score (Factor 1) in projection was strongly correlated with data set. The concentration of target object and Factor 1 could be fitted by replacing sample points in LDA plot with different concentrations of the same sample. As illustrated in **Figure S25**, HCA results demonstrated that the accuracy of prediction and classification for Cr^{3+} solutions with different concentrations (0-30 μM) reached 100%. In LDA score map, Factor 1 was identified with an impressively high correlation coefficient of 98.07%. Factor 1 was equipped with Cr^{3+} concentration, yielding a regression curve and a correlation equation with a correlation coefficient of 0.985. Similar quantitative results of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ were also obtained in **Figure S26 and S27**). The detection limits (LOD) of Cr^{3+} , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ were 1.99, 3.28, and 1.29 μM , respectively. According to the standards of U.S. Environmental Protection Agency (EPA) and World Health Organization (WHO), the total chromium content (including Cr(III) and Cr(VI)) in drinking water should not exceed 0.1 and 0.05 mg/mL. The LODs for chromium

speciation were converted to 0.1034 mg/mL, 0.3804 mg/mL, and 0.2786 mg/mL, respectively. Experiment results of three Cr speciation and poly-mixtures were found in **Table S2**.

The performance of this sensor array for multi-component samples was also evaluated. As shown in **Figure S28-S30**, taking $\text{Cr}^{3+}+\text{CrO}_4^{2-}$ as an example, the corresponding classification accuracy of HCA was 100%. In LDA score map, distinct interclass separation was observed among different mixing proportions. Notably, while a subset of data points from 1:9 ratio group overlapped with 0:1 ratio group's confidence interval, the confusion matrix demonstrated 92.5% classification accuracy. Similarly, the classification accuracy of $\text{Cr}^{3+}+\text{Cr}_2\text{O}_7^{2-}$ could reach 100% according to **Figure S29**. As revealed in **Figure S30**, HCA achieved 100% accuracy in classification analysis, while LDA maintained a recognition accuracy of 97.5% using output matrix. Three-component system could be regarded as an additional introduction of Cr^{3+} into two-component system of Cr (VI) (**Figure S31**). It was worth noting that the degree of inter-class dispersion had increased again for each sample proportion in score maps, and the corresponding accuracy had increased to 98%.

Three Cr speciation had a good linear relationship ranging from 0 to 60 μM . Thus, the intensity of three two-component groups was measured with 1:1, 1:4, and 4:1 ratios. The regression equation was fitted after HCA and LDA analysis. As depicted in **Figure S32-34**, a strong linear correlation was observed at concentrations below 60 μM across samples with different proportions. However, it should be noted that

similar properties of CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ made it difficult to distinguish them, and the lowest LOD was only 12.83 μM (**Table S2**). Finally, quantitative analysis of three-component samples was carried out in a mixing ratio of 1:1:1 (**Figure S35**), showing a LOD of 10.19 μM in the range of 0-60 μM . This dual-emission fluorescence sensor array has great potential in both specific recognition and quantitative detection of Cr speciation.

The sensor array was also used in real samples (**Figure 4B-4C**). The dendrogram of HCA analysis could classify data groups of different Cr speciation correctly. The distribution of data classes was also clear enough according to LDA, indicating this method could effectively identify different Cr distribution in real waters. Besides, the sensor array could also be used to detect other real samples in the environment. As shown in **Figure S37**, when the target concentration was 0-20 μM , it was feasible to quantitatively detect Cr^{3+} , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ by simulating real water samples. Besides, the analytical performance in river water was also tested. The recovery and relative standard deviations (RSD) were listed in **Table S3 and S4**.

■ CONCLUSIONS

Integrating with machine learning, our study developed a novel dual-emission fluorescence sensor array for Cr speciation analysis with high selectivity and sensitivity. The fluorescence probe exhibited high selectivity and sensitivity to detect Cr^{3+} , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$. Besides, machine learning correlated fluorescence signals with target concentrations by iteratively analyzing potential correlation factors, achieving accurate distinction between Cr (III) and Cr (VI) in single or multi-

component samples. Besides, this sensor array showed a low detection limit, overcoming limitations of traditional sensor arrays with qualitative analysis. These findings were expected to provide a feasible idea for metal speciation analysis in drinking water.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the web.

Chemicals and materials; preparation of MSN-NH₂, GSH-Au NCs, and GSH-AgAu NCs; calculation of quenching constant and quenching rate constant; XPS spectrum and SEM images of MSN@Zr@Au and MSN@Zr@AgAu; changes in pH and NaCl; UV-vis spectra; effects of cationic; quenching constant and quenching rate constant of different Cr speciation; formulas for quantitative detection of Cr speciation (PDF)

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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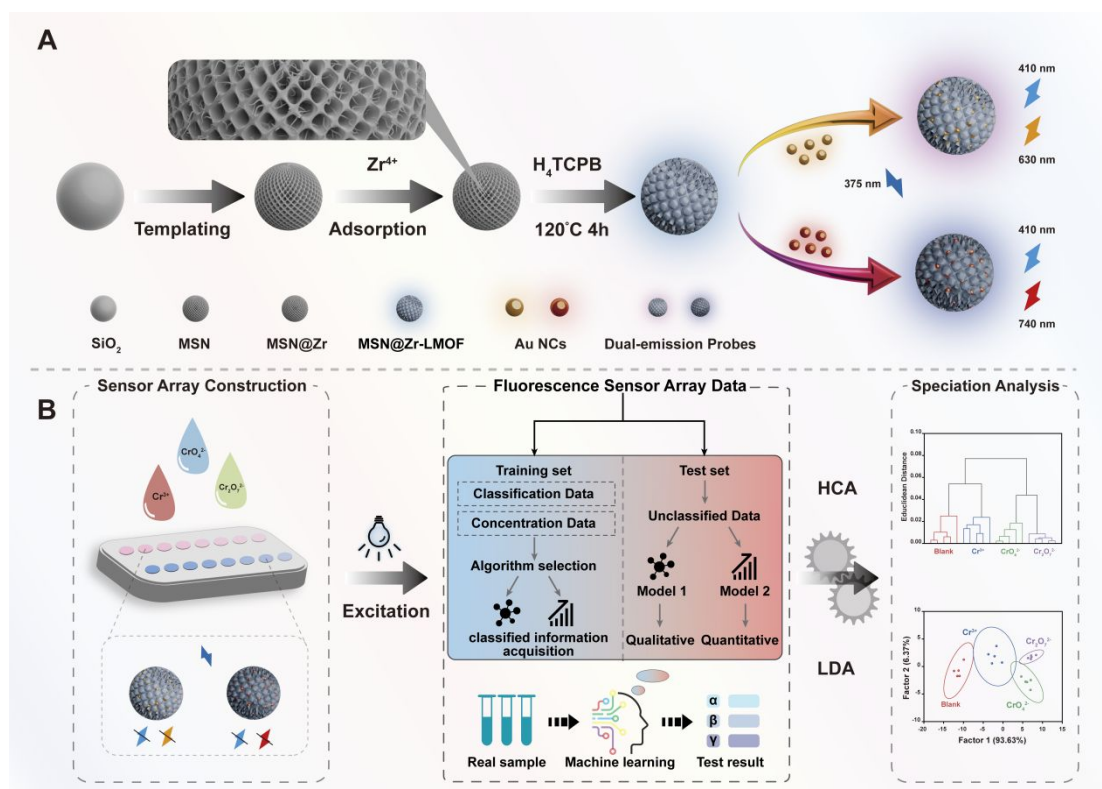
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400



Scheme 1. Schematic Illustration of (A) Synthesis of MSN@Zr@Au/AgAu and (B) Development of this dual-emission fluorescence sensor array for the analysis of Cr speciation.

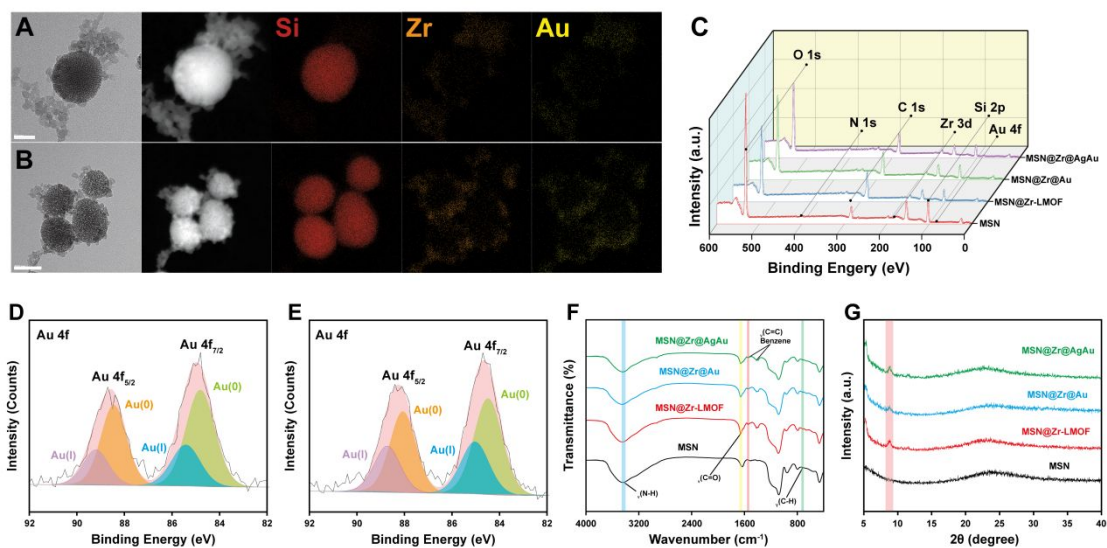


Figure 1. HRTEM images and elemental mapping profiles for Si, Zr, and Au elements of (A) MSN@Zr@Au (Scale bar: 50 nm) and (B) MSN@Zr@AgAu (Scale bar: 100 nm); The XPS full spectrum of (C) MSN, MSN@Zr-LMOF, MSN@Zr@Au, MSN@Zr@AgAu, and the Au 4f region of (D) MSN@Zr@Au, (E) MSN@Zr@AgAu; (F) FT-IR spectra and (G) XRD patterns of MSN, MSN@Zr-LMOF, MSN@Zr@Au, MSN@Zr@AgAu.

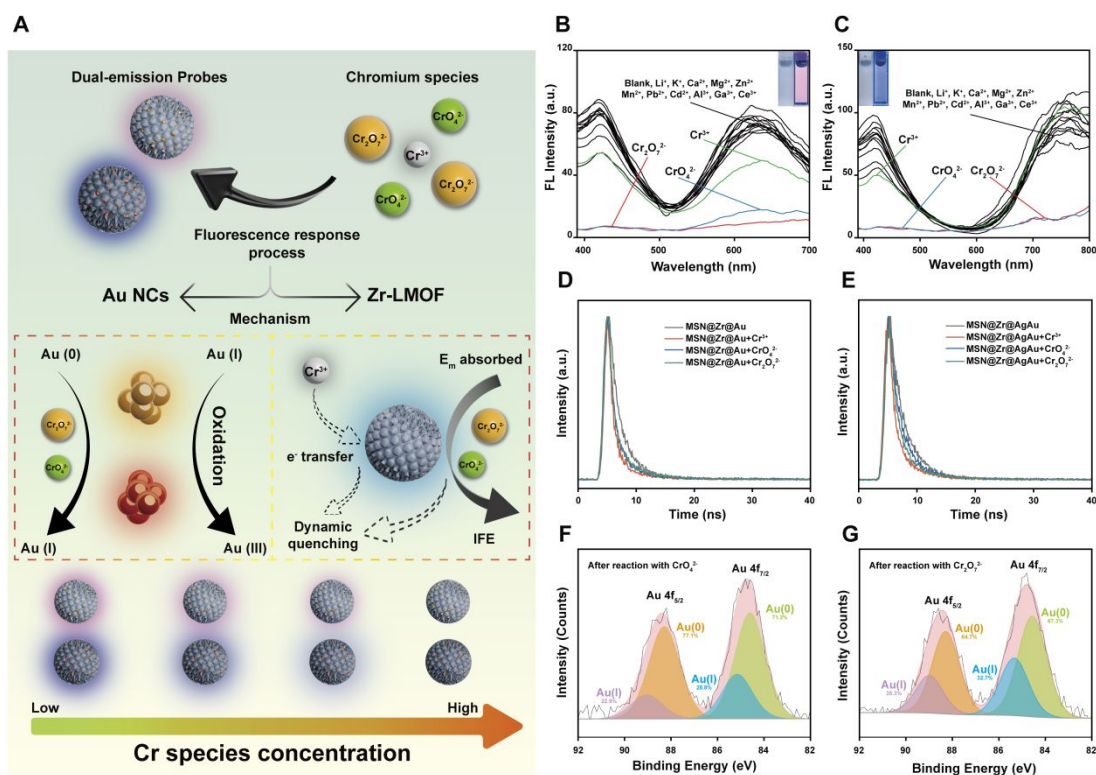


Figure 2. The illustration of (A) fluorescence quench mechanism of MSN@Zr@Au/AgAu. (B-C) Response curves of different Cr speciation to MSN@Zr@Au/AgAu. Fluorescence lifetime decay curves of (D) MSN@Zr@Au, (E) MSN@Zr@AgAu reacted with Cr^{3+} , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. The XPS spectra of Au 4f region of MSN@Zr@Au reacting with (F) CrO_4^{2-} and (G) $\text{Cr}_2\text{O}_7^{2-}$.

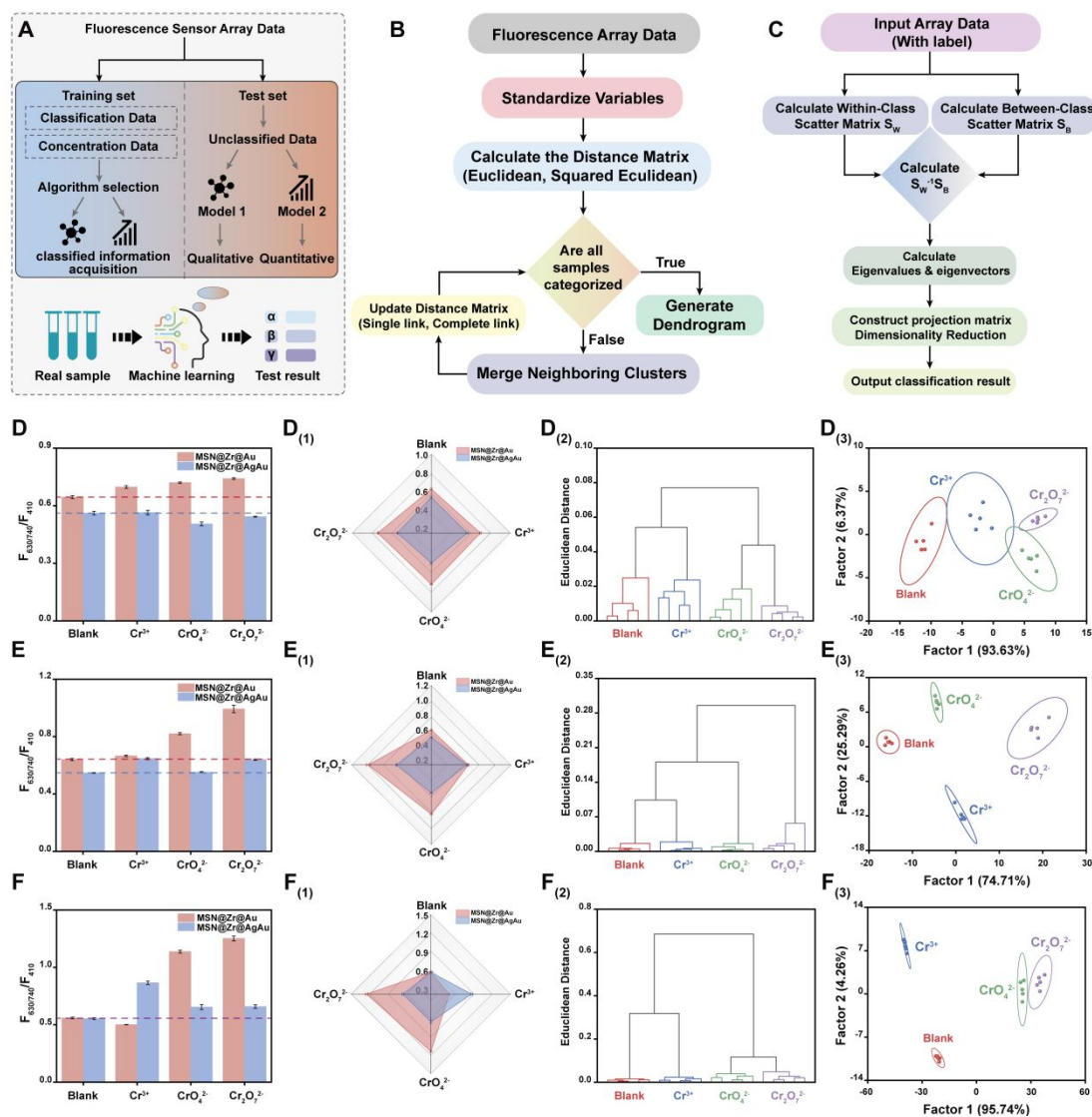


Figure 3. (A) Schematic diagram of the classification prediction of chromium species by machine learning. (B) Diagram of the HCA classification process. (C) Diagram of the LDA classification process. (D-D₍₃₎) Fingerprint, radar plot, HCA plot and LDA canonical score plot for the dual-emission sensor array against Cr^{3+} , CrO_4^{2-} and $Cr_2O_7^{2-}$ (all at 1 μ M). (E-E₍₃₎) and (F-F₍₃₎) The concentrations of chromium species are 10 μ M and 50 μ M, respectively.

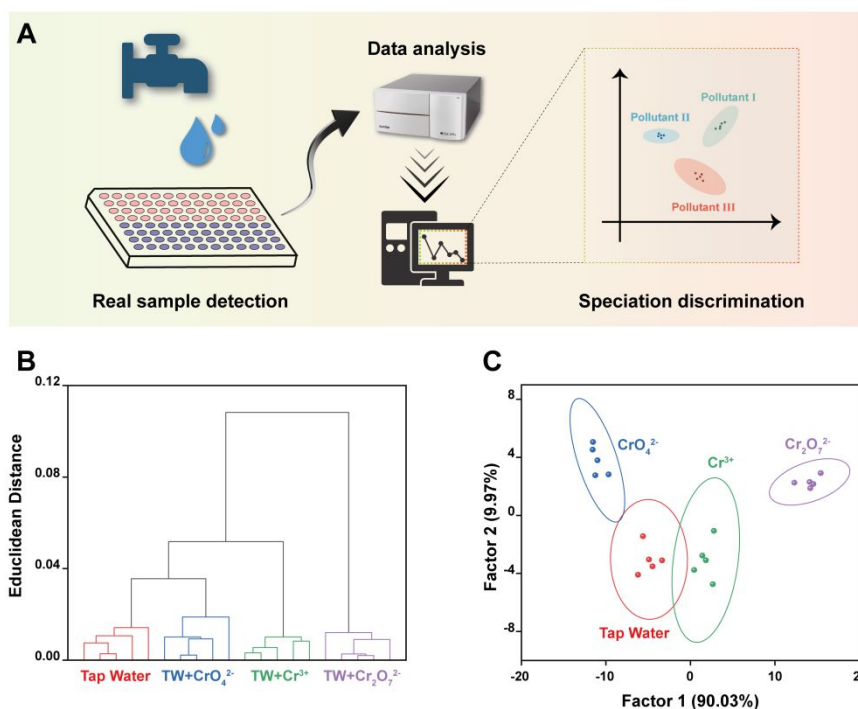
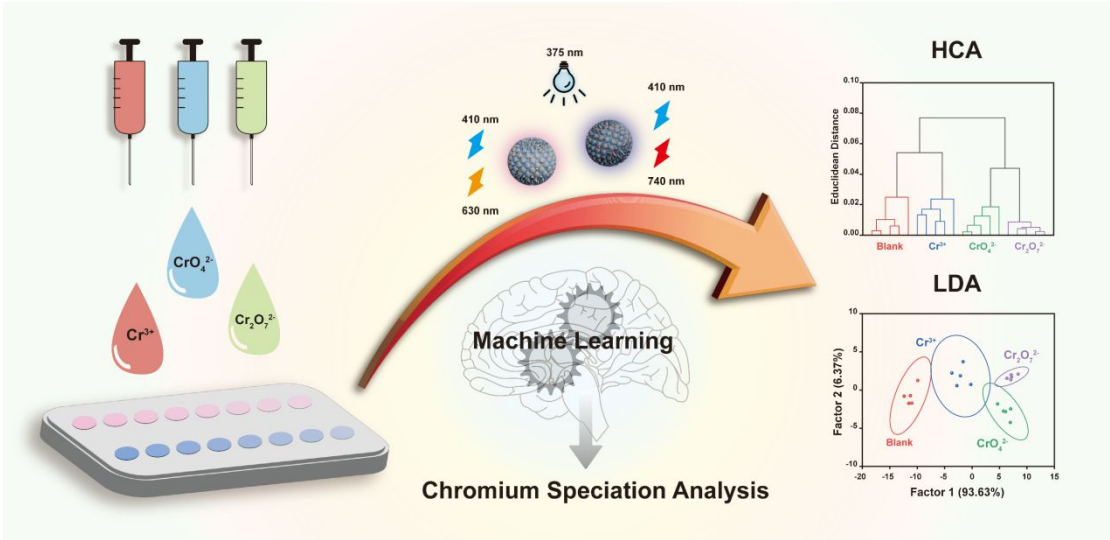


Figure 4. (A) Illustration diagrams of the dual-emission sensor array to detect real samples for Cr speciation discrimination. (B) HCA plot and (C) LDA canonical score plot for the discrimination of four tap water samples spiked by different Cr speciation (all at 10 μ M) using the sensor array.

Chromium Speciation Monitoring Platform for Drinking Water: Machine Learning Assisted Dual-Emission Fluorescence Sensor Array

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Jingfu Liu³, Zhen Zhang^{1*}

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Supporting Information

Chromium Speciation Monitoring Platform for Drinking Water: Machine Learning Assisted Dual-Emission Fluorescence Sensor Array

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S.1 Material and Apparatus

Hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$) and AgNO_3 were obtained from Shanghai Sangon Biotechnology Co., Ltd. (Shanghai, China). Glutathione (GSH), Benzoic acid, hexadecyltrimethylammonium bromide (CTAB), and ZrCl_4 were purchased from Aladdin Reagent Co. (Shanghai, China). Tetraethyl orthosilicate (TEOS), 3-Aminopropyltriethoxysilane (APTES), and 1,2,4,5-Tetrakis(4-carboxyphenyl)benzene (H_4TCPB) were acquired from Shanghai Macklin Biochemical Technology Co., Ltd. All other chemicals and solvents were of analytical grade or the highest purity available. All solutions were prepared with deionized water.

S.2 Instrumentation

Fluorescence spectra were recorded on a Thermo Lumina fluorescence spectrophotometer (Thermo, USA). UV–Visible (UV–vis) absorption spectra were recorded on a UV-2600 scanning spectrophotometer using a 1 cm quartz cuvette (Shimadzu, Japan). The particle size was analyzed using a JEM 2100 Transmission Electron Microscopy (TEM) (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) analysis was performed using an ESCALAB 250 XI electron spectrometer (Thermo, USA). FT-IR spectra were obtained using a 16 Bruker IFS66V FT-IR spectrometer (Germany). X-ray Diffraction (XRD) analysis was performed using a D8 ADVANCE (Bruker, Germany). The collected data matrices were treated with hierarchical cluster analysis (HCA) and linear discriminant analysis (LDA) using SPSS (version 26.0).

S.3 Synthesis of MSN-NH₂

The preparation of MSN-NH₂ was carried out according to a previous procedure with slight modifications.¹ First, an aqueous solution of CTAB (7.1 mg/mL, 70 mL) was mixed with 0.8 mL of NH_4OH and 10 mL of ethanol and stirred vigorously at

room temperature for 30 min. Then, 2.5 mL of TEOS and 250 μ L of APTES were added to the mixture and continued stirring for 4 h. The final solution was centrifuged (8000 rpm, 5 min) with ethanol 3 times. To remove the template CTAB, the precipitation after centrifugation was ultrasonically dispersed in a mixture of HCl/ethanol and refluxed at 70 $^{\circ}$ C for 10 h. The obtained solution was alternately washed 3 times with deionized water and ethanol (8000 rpm, 5 min), and the final product was vacuum dried at 60 $^{\circ}$ C for further use.

S.4 Synthesis of GSH-Au NCs

The synthesis process of GSH-Au NCs was scaled up based on previous studies.² The GSH aqueous solution (24.0 mL, 10 mM) was mixed with HAuCl₄ (1.6 mL, 100 mM) and stirred for 5 min at room temperature. The deionized water (54.4 mL) was added to the above system and stirred for 24 h at 70 $^{\circ}$ C. The final obtained GSH-Au NCs were collected and stored at 4 $^{\circ}$ C for further use.

S.5 Synthesis of GSH-AgAu NCs

The synthesis of GSH-AgAu NCs was according to the previous study with some modifications.³ First, an aqueous solution of GSH (100 mM, 0.182 mL) was mixed with HAuCl₄ (0.5 mL, 30 mM) in 10 mL of deionized water. Then, AgNO₃ aqueous solution (20 mM, 0.2 mL) was added to the mixture and stirred at room temperature for 5 min, and then the NaOH (0.2 M, 0.7 mL) was added subsequently. The mixture was then transferred to an oil bath and preheated to 115 $^{\circ}$ C under magnetically stirring for 20 min. When the color of the mixture turned reddish brown, the solution was collected after cooling to room temperature and stored at 4 $^{\circ}$ C for future use.

S.6 Surface functionalization of MSN-NH₂ with Zr-LMOF

The process of anchoring Zr⁴⁺ on the surface of mesoporous silica microspheres

is based on previous studies with minor modifications.⁴⁻⁶ In detail, 200 mg of MSN-NH₂ and 15 mg of ZrCl₄ were mixed into a round-bottomed flask using 10 ml of deionized water and 20 ml of DMF for ultrasonic dispersion, stirring for 1 h to adsorb Zr⁴⁺. Then, 21 mg of H₄TCPB and 500 mg of benzoic acid were added to the above system. After ultrasonic processing for 1 min, the round-bottom flask was transferred to an oil bath at 120 °C for 4 h. The final solution was alternately washed and centrifuged 3 times with DMF/methanol to remove the unreacted substance, the precipitation of MSN@Zr-LMOF was redispersed in 9 mL of deionized water for use.

S.7 Fluorescence lifetime analysis

Fluorescence lifetime analysis was performed using an FLS980 fluorescence spectrometer (Edinburgh, UK). under 375 nm light source excitation, the fluorescence decay time (nanosecond level) of the hybridized fluorescent material was measured. The fast decay time (τ_1) and slow decay time (τ_2) were fitted and exported by Edinburgh instrument, which used for subsequent calculations of the fluorescence quenching mechanism. The fluorescence lifetime decay times were shown in **Table S5**.

S.8 Calculation of quenching constant and quenching rate constant

The fluorescence quenching process follows the Stern-Volmer equation (Eq. 1).

$$F_0/F = 1 + K_{sv}C_q = 1 + K_q\tau_0C_q \quad (1)$$

The F_0 represents the fluorescence intensity of the fluorescence probe without targets and the F represents the fluorescence intensity of the probe with different Cr speciation at the optimal emission peak, respectively. The K_{sv} is the quenching

constant, C_q represents the concentration of Cr speciation, K_q is the quenching rate constant, and τ_0 represents the fluorescence lifetime of the probe before the reaction. The maximum dynamic quenching constant of the standard quenchers on the fluorescent substance is about $2 \times 10^{10} \text{ L} \cdot \text{M}^{-1} \cdot \text{s}^{-1}$, the type of quenching can be preliminarily identified by the constant. The calculation results were listed in **Table S1**.

S.9 Establishment of array sensor for Cr discrimination

To establish the fluorescence array sensor, 100 μL of different Cr speciation (Cr^{3+} , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$) was introduced into 20 μL of two fluorescent sensor probes, including MSN@Zr@Au and MSN@Zr@AgAu . After incubating at room temperature for 5 min, the fluorescence spectra of the mixture were recorded, and the fluorescence intensity of these two probes under 375 nm excitation was measured at emission peaks of 410 nm, 630 nm, and 740 nm, respectively, to distinguish different Cr speciation. This process was repeated five times for 3 kinds of Cr speciation and then generated a set of 2 channels $\times$ 3 Cr $\times$ 5 repetitions of the training data matrix. Meanwhile, to remove the influence of potential interference factors on the signal intensity, the raw data were normalized by F_{630}/F_{410} or F_{740}/F_{410} , where F_{630} and F_{740} represent the Au NCs fluorescence intensity of the mixture after reaction with different Cr speciation, and F_{410} represents the Zr-LMOF fluorescence intensity. All data matrices were processed by SPSS, and experimental results were obtained by linear discriminant analysis (LDA) and hierarchical cluster analysis (HCA). Fluorescence response patterns and heat maps of different MSN@Zr@Au and

MSN@Zr@AgAu for detecting different Cr speciation were generated by Origin processing.

S.10 Confusion matrix analysis

Combined with the classification results of the intelligent algorithm, the original mixing ratio was further recorded as the original class. The group by LDA classification was recorded as the prediction class, and the confusion matrix could be drawn to calculate the classification accuracy of the sensor array. When the actual class of the sample was positive and the sensor array also identified it as positive, the sample points were recorded as true class (TC). Otherwise, it was considered a false class (FC). The accuracy calculation formula of the sensor array with the classification algorithm could be obtained: $TC/(TC+FC)*100\%$.

S.11 Real sample analysis

Tap water (taken from Jiangsu University) and river water (taken from Tuanjie River, Zhenjiang, Jiangsu Province) samples were collected and analyzed. The Cr^{3+} , CrO_4^{2-} , and $Cr_2O_7^{2-}$ with a final concentration of 10 μM were added, and the tap water without targets was used as a blank group. A recovery experiment was performed to study the accuracy and stability of this sensor assay. A certain concentration solution of Cr^{3+} (8 μM), CrO_4^{2-} , and $Cr_2O_7^{2-}$ (16 μM) was added to three sets of real samples respectively (labeled as Sample 1, Sample 3, and Sample 5). Sample 2, Sample 4, and Sample 6 were obtained by diluting at a ratio of 1/2. These six samples were detected using the sensor array and calculated by the corresponding equation.

S.12 Anti-interference capability

The purified water was used as the detection environment to evaluate the anti-interference performance of the sensor array. Firstly, an interfering ion, at a concentration three times higher than the target (150 μM), was added to the array system containing the target at 50 μM . The test results were shown in **Figure S36**.

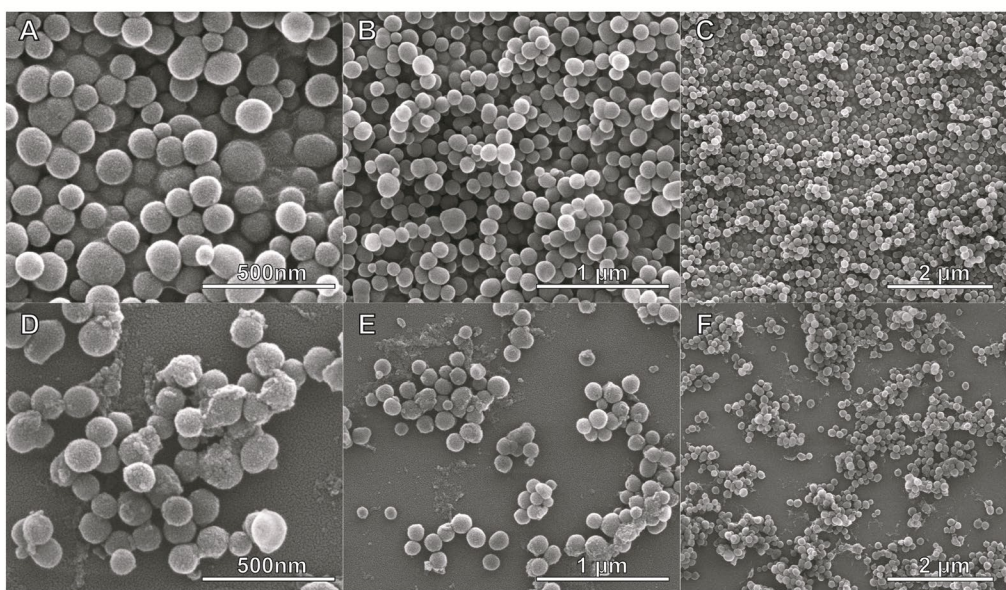


Figure S1. SEM images of (A)-(C) MSN and (D)-(F) MSN@Zr-LMOF in different scales.

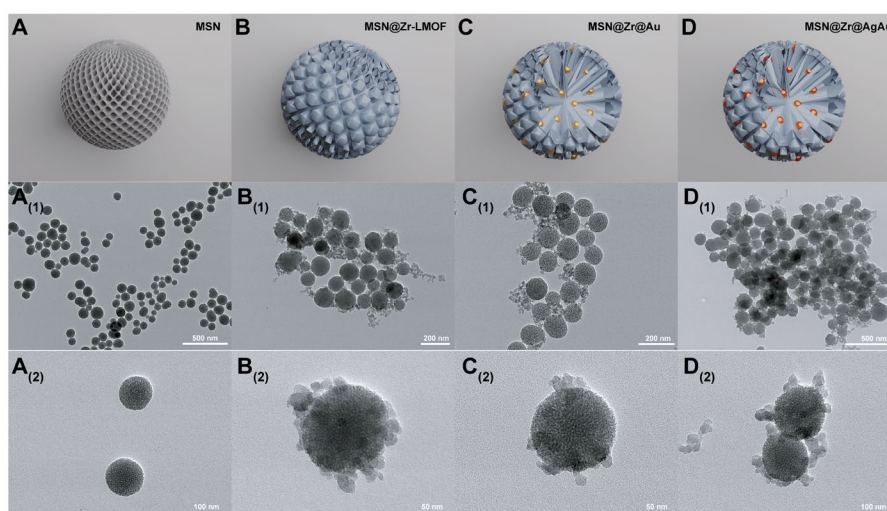


Figure S2. Three-dimensional (3D) model of (A) MSN, (B) MSN@Zr-LMOF, (C) MSN@Zr@Au, and (D) MSN@Zr@AgAu. (A₍₁₎-D₍₁₎) The corresponding TEM images (Scale: 200-500 nm) and (A₍₂₎-D₍₂₎) monodisperse TEM images (Scale: 50-100 nm).

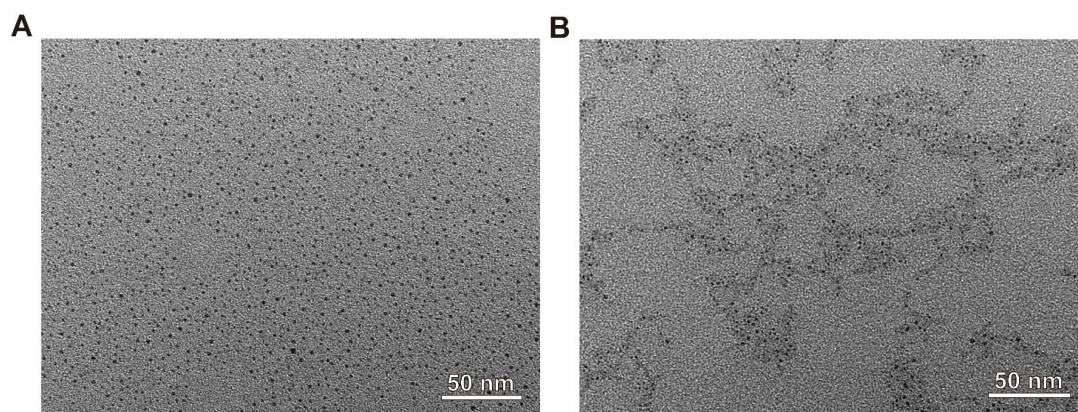


Figure S3. TEM images of Au NCs. (A) GSH-Au NCs, (B) GSH-AgAu NCs.

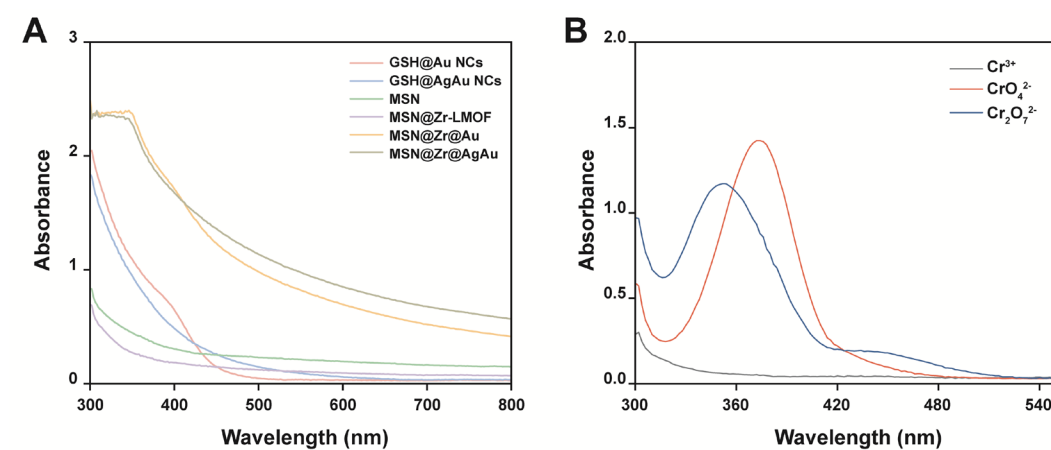


Figure S4. UV-vis absorption of (A) Probes and (B) 3 kinds of Cr species.

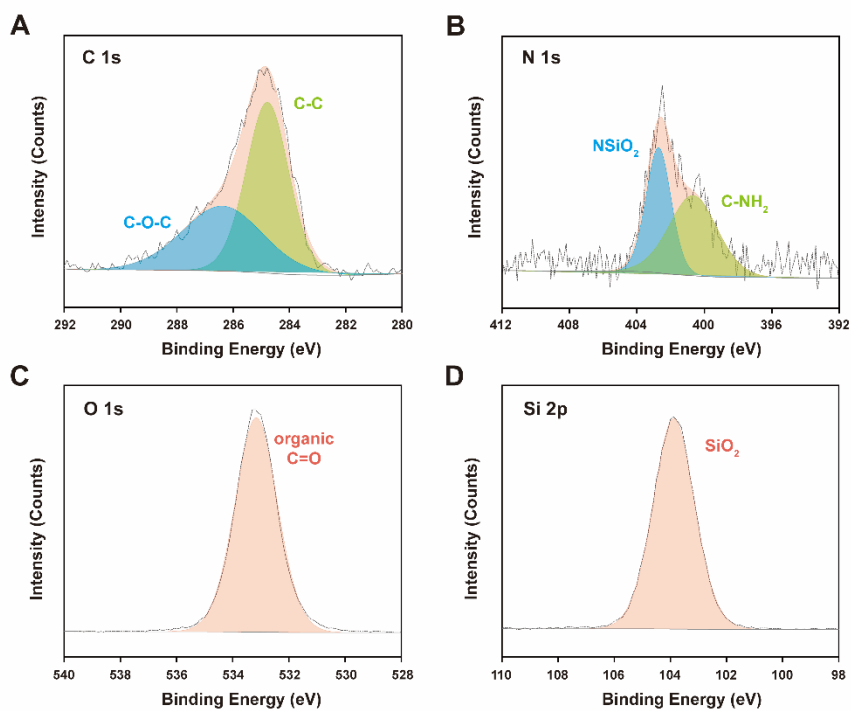


Figure S5. XPS spectrum of MSN. (A) C 1s, (B) N 1s, (C) O 1s and (D) Si 2p.

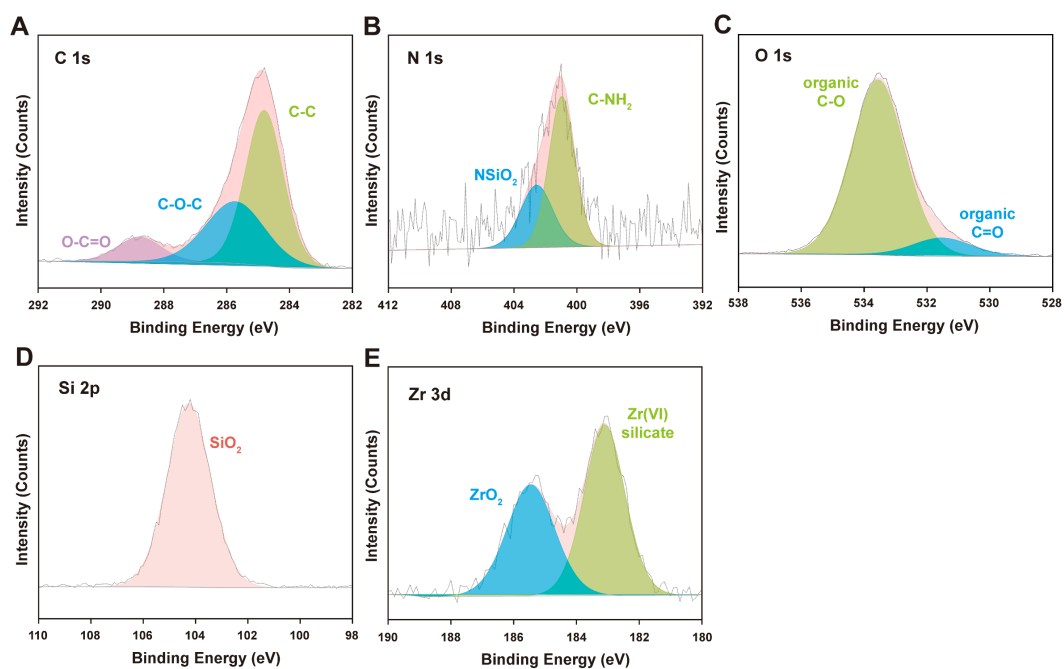


Figure S6. XPS spectrum of MSN@Zr-LMOF. (A) C 1s, (B) N 1s, (C) O 1s, (D) Si 2p and (E) Zr 3d.

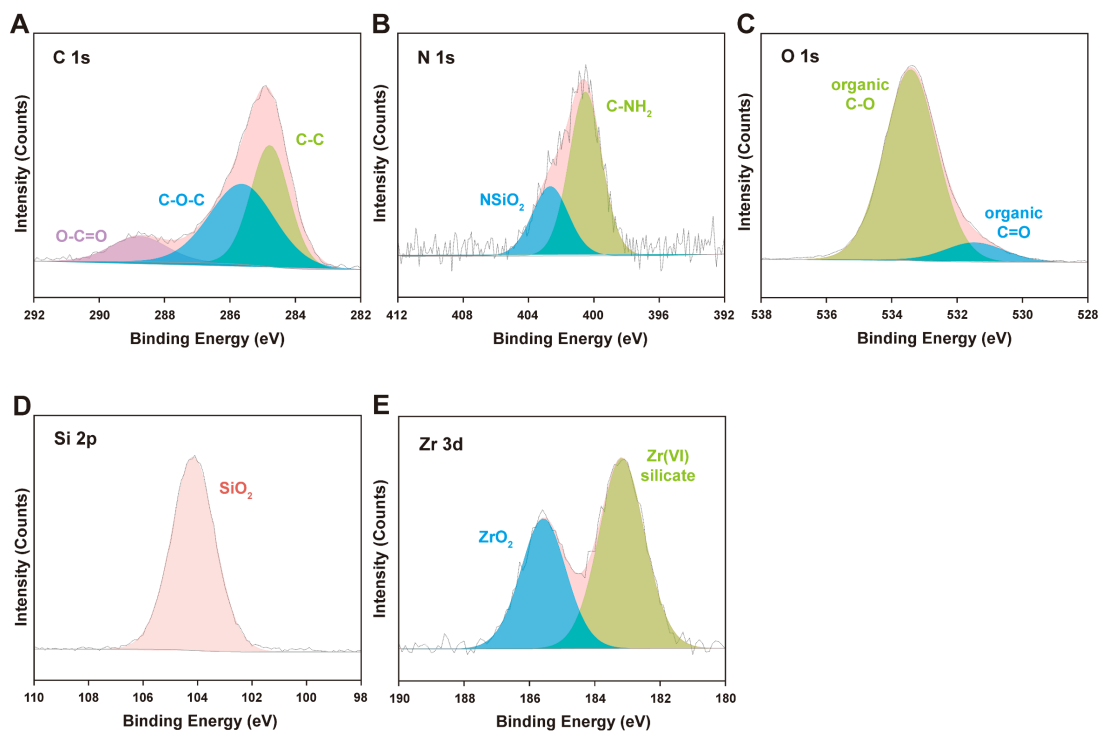


Figure S7. XPS spectrum of MSN@Zr@Au. (A) C 1s, (B) N 1s, (C) O 1s, (D) Si 2p and (E) Zr 3d.

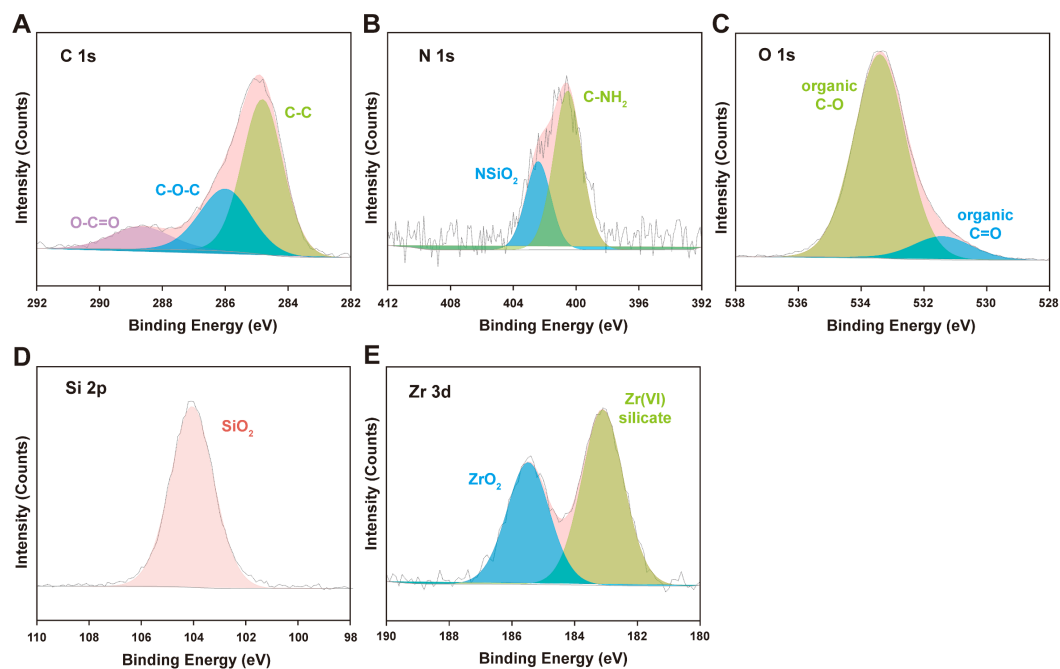


Figure S8. XPS spectrum of MSN@Zr@AgAu. (A) C 1s, (B) N 1s, (C) O 1s, (D) Si 2p and (E) Zr 3d.

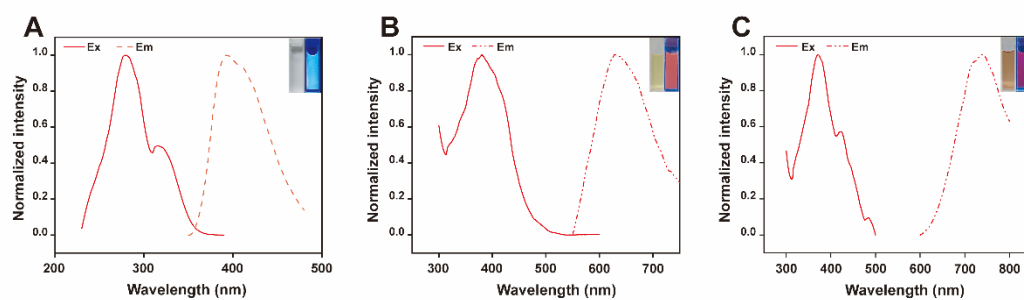


Figure S9. Excitation and emission spectra of (A) MSN@Zr-LMOF, (B) GSH-Au NCs, and (C) GSH-AgAu NCs. The insets are photographs of the MSN@Zr-LMOF and Au NCs under visible light (left) and 365 nm UV irradiation (right).

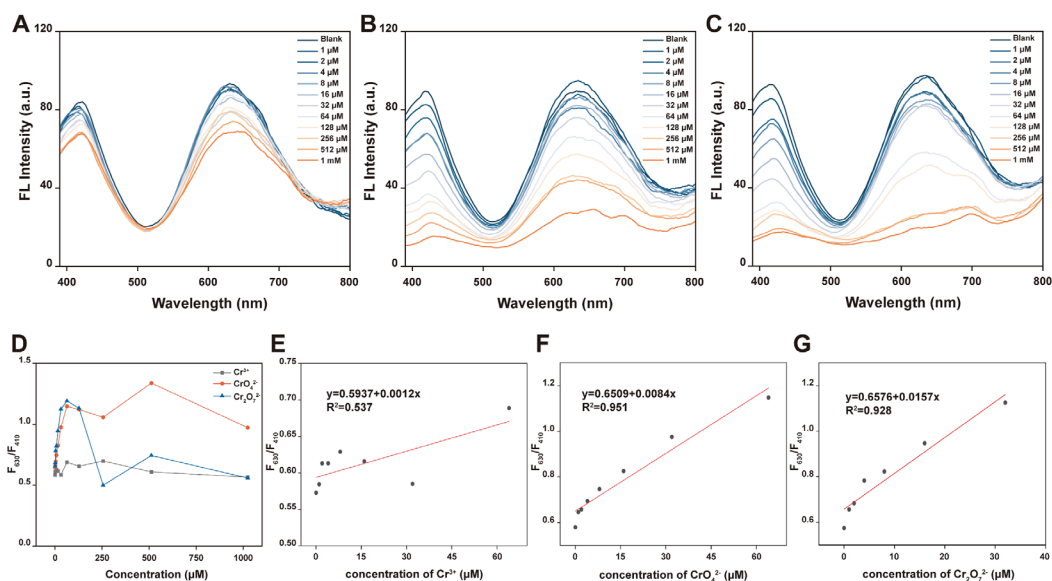


Figure S10. The fluorescence spectra of MSN@Zr@Au with (A) Cr³⁺, (B) CrO₄²⁻ and (C) Cr₂O₇²⁻ with different concentrations. (D) It is the ratio of fluorescence intensity at 630 nm to 410 nm under different Cr concentrations. (E-G) Linear relationship between chromium species concentration and fluorescence intensity ratio.

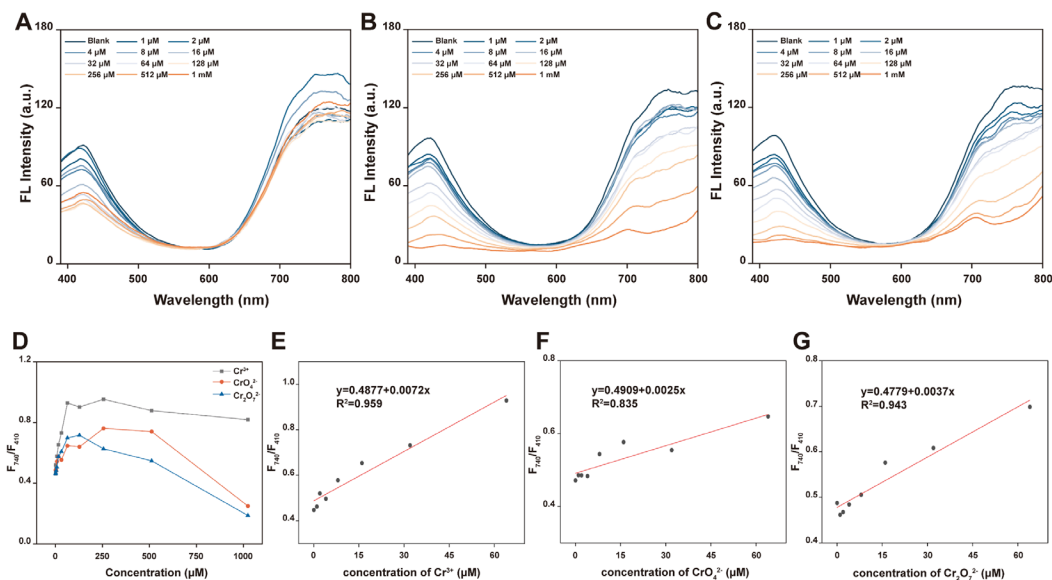


Figure S11. The fluorescence spectra of MSN@Zr@AgAu with (A) Cr³⁺, (B) CrO₄²⁻ and (C) Cr₂O₇²⁻ with different concentrations. (D) is the ratio of fluorescence intensity at 740 nm to 410 nm under different Cr concentrations. (E-G) Linear relationship between chromium species concentration and fluorescence intensity ratio.

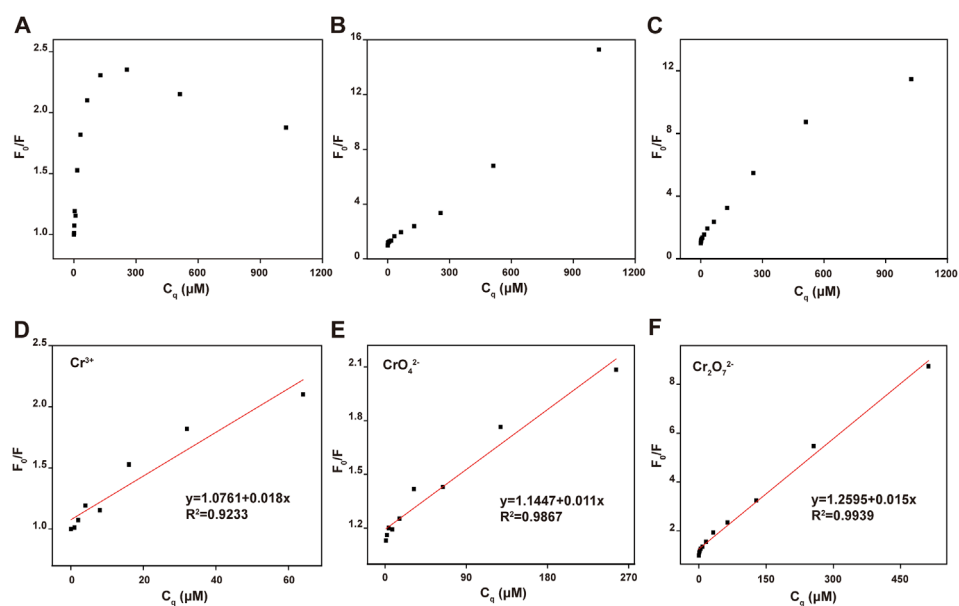


Figure S12. Scatter graph of MSN@Zr@Au NCs reacted with (A) Cr^{3+} , (C) CrO_4^{2-} , (E) $\text{Cr}_2\text{O}_7^{2-}$ in 410 nm and corresponding Stern-Volmer curves.

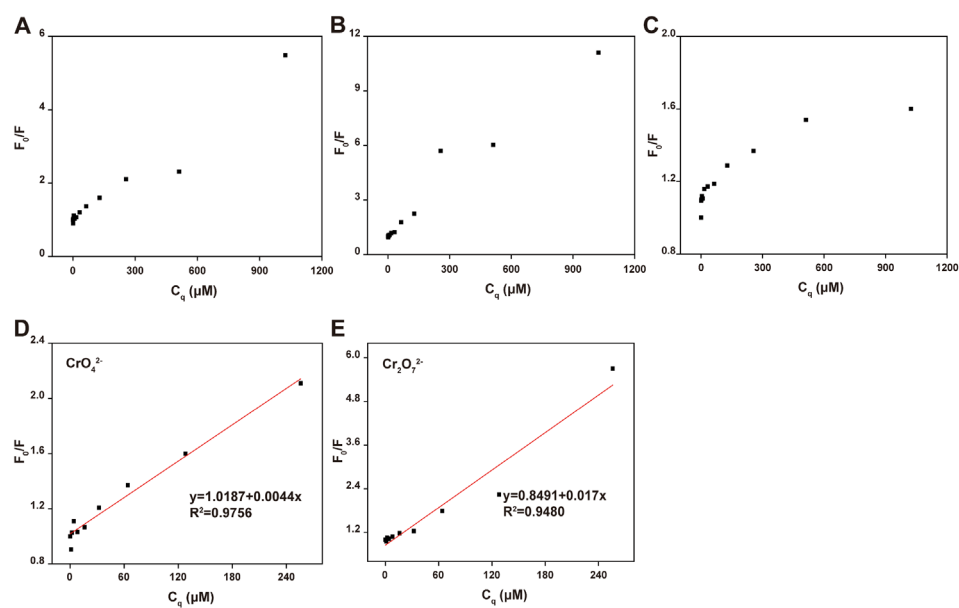


Figure S13. Scatter graph of MSN@Zr@Au reacted with (A) CrO_4^{2-} , (B) $\text{Cr}_2\text{O}_7^{2-}$, (C) Cr^{3+} in 630 nm and corresponding Stern-Volmer curves.

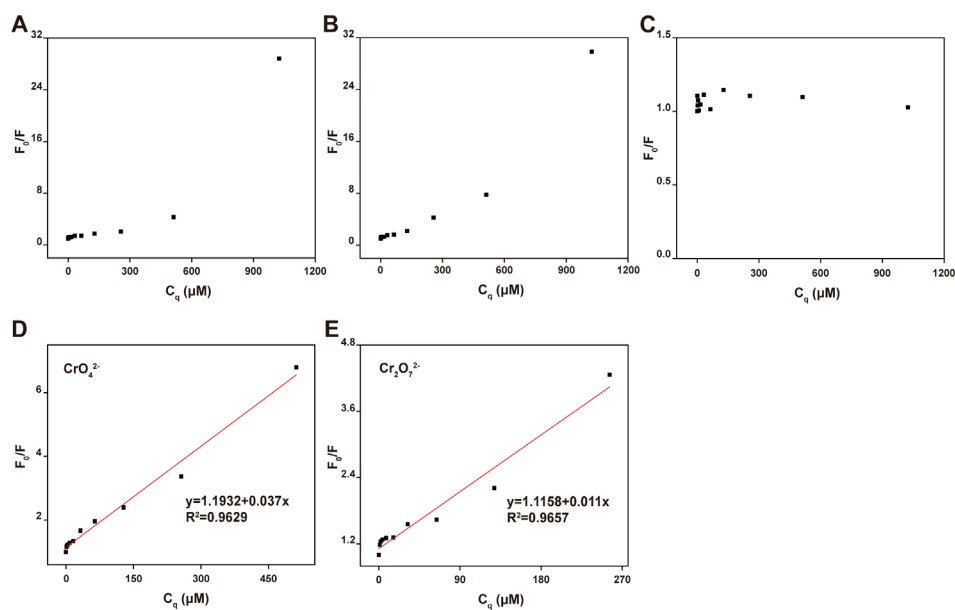


Figure S14. Scatter graph of MSN@Zr@AgAu reacted with (A) CrO_4^{2-} , (B) $\text{Cr}_2\text{O}_7^{2-}$, (C) Cr^{3+} in 740 nm and corresponding Stern-Volmer curves.

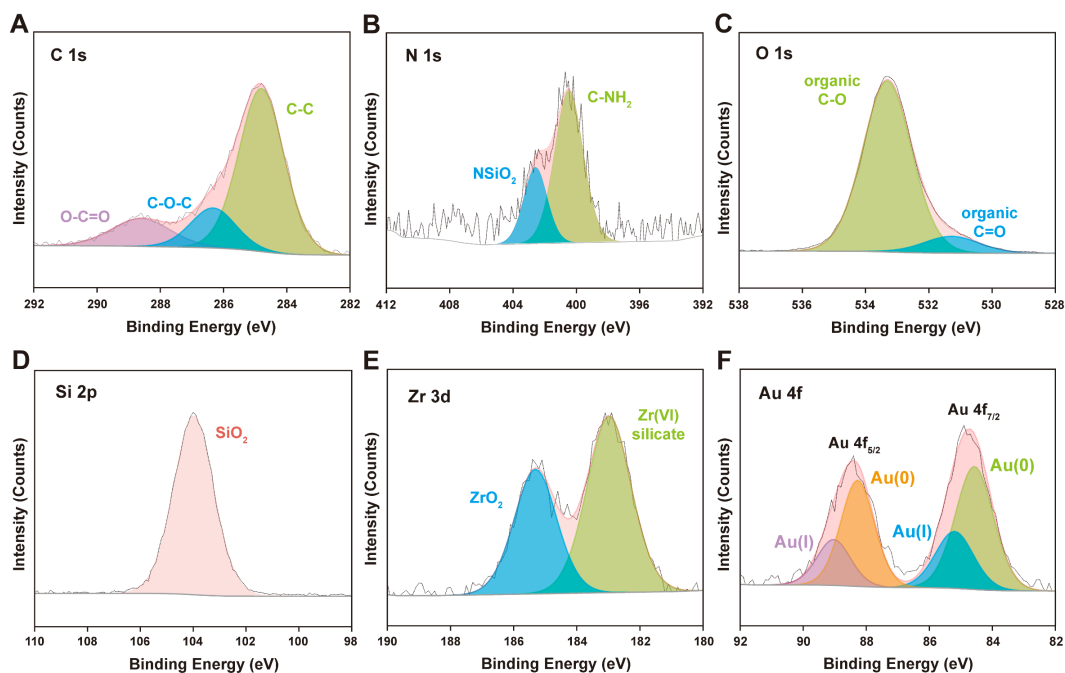


Figure S15. XPS spectrum of MSN@Zr@Au reacted with Cr^{3+} . (A) C 1s, (B) N 1s, (C) O 1s, (D) Si 2p, (E) Zr 3d and (F) Au 4f.

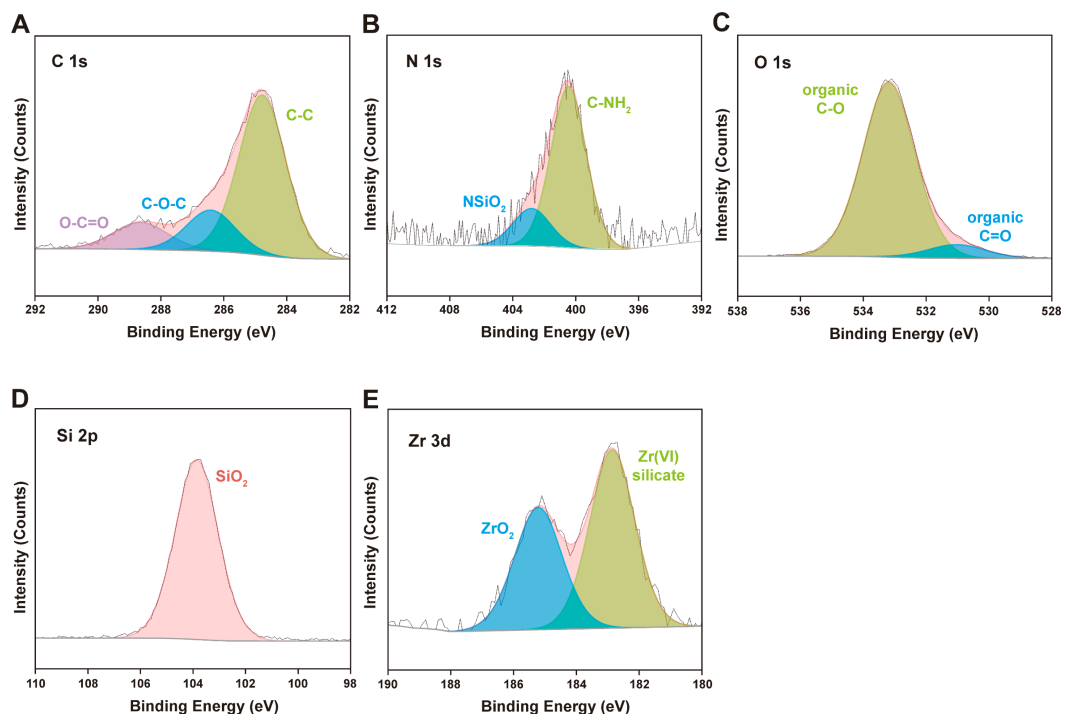


Figure S16. XPS spectrum of MSN@Zr@Au reacted with CrO_4^{2-} . (A) C 1s, (B) N 1s, (C) O 1s, (D) Si 2p and (E) Zr 3d.

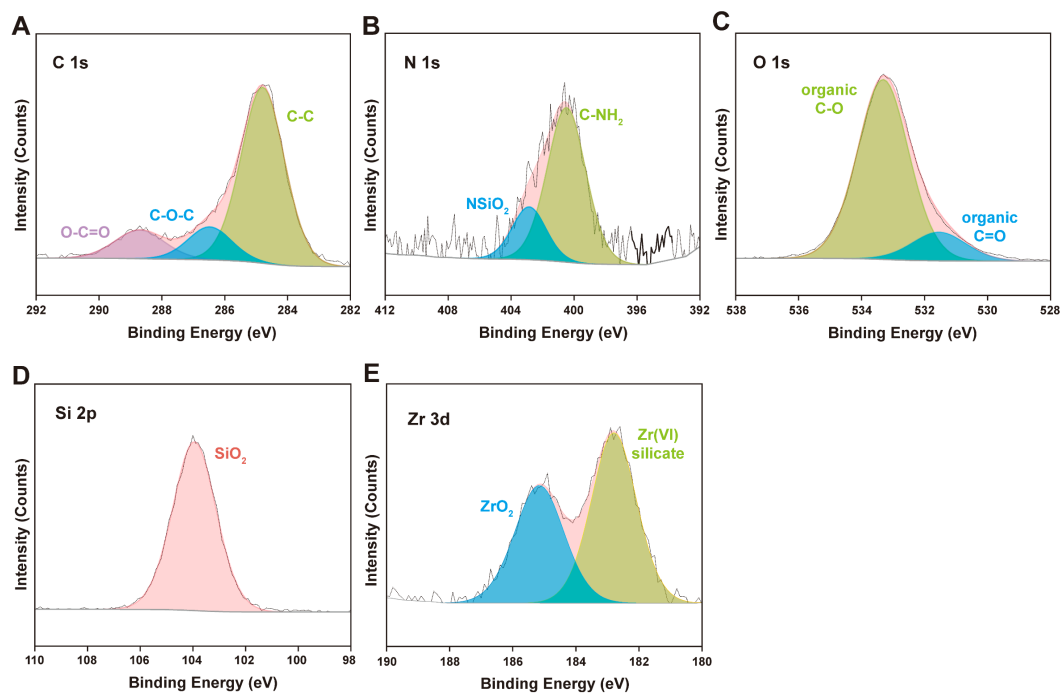


Figure S17. XPS spectrum of MSN@Zr@Au reacted with $\text{Cr}_2\text{O}_7^{2-}$. (A) C 1s, (B) N 1s, (C) O 1s, (D) Si 2p and (E) Zr 3d.

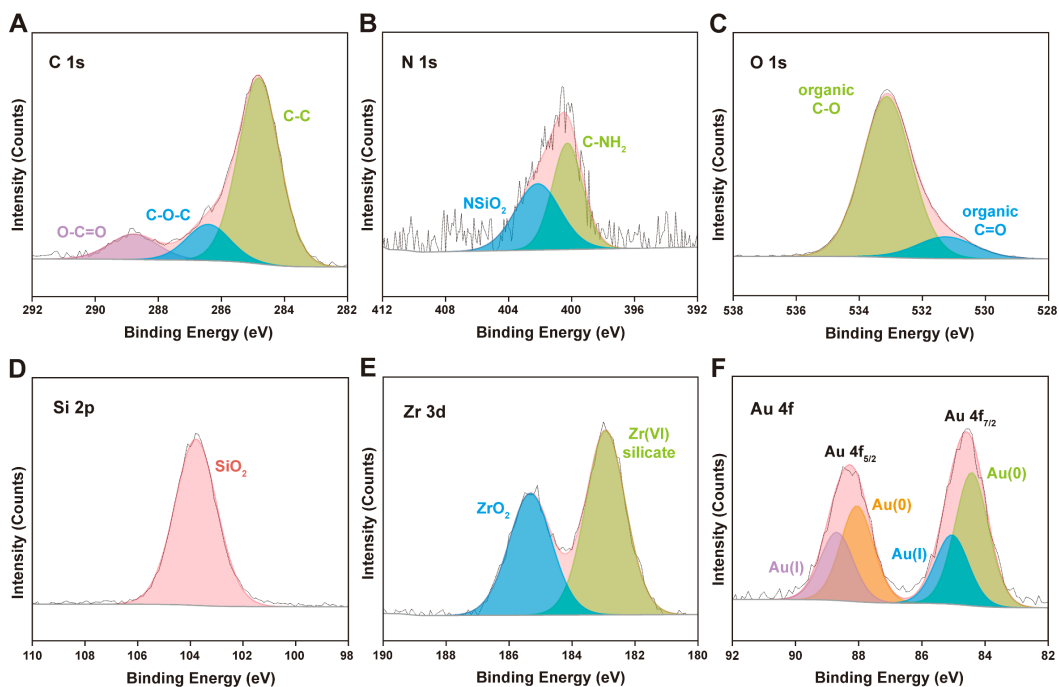


Figure S18. XPS spectrum of MSN@Zr@AgAu reacted with Cr^{3+} . (A) C 1s, (B) N 1s, (C) O 1s, (D) Si 2p, (E) Zr 3d and (F) Au 4f.

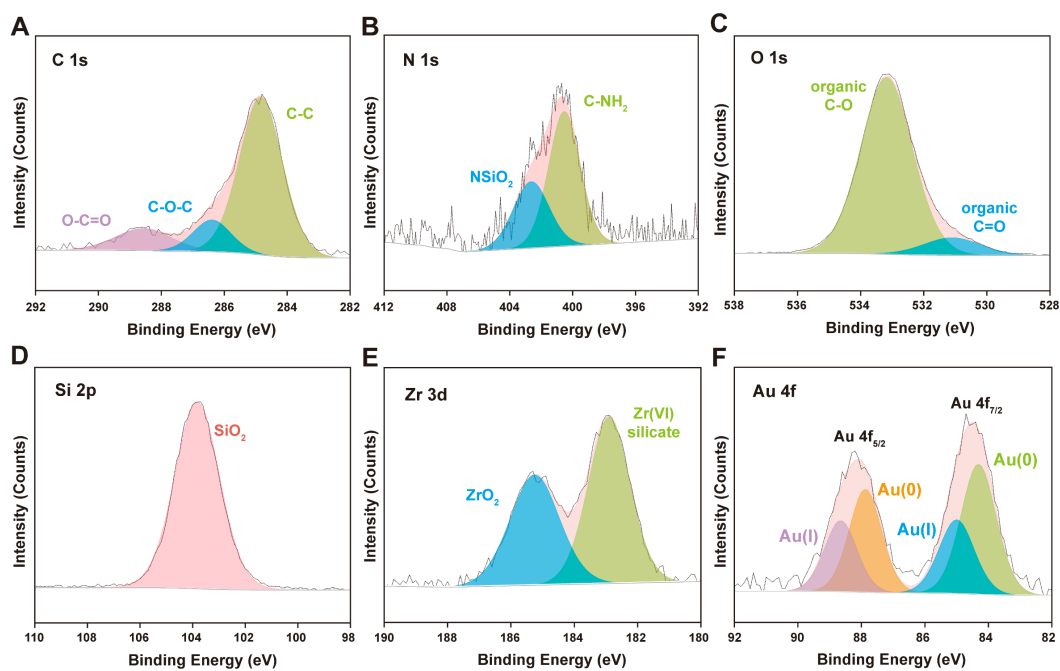


Figure S19. XPS spectrum of MSN@Zr@AgAu reacted with CrO_4^{2-} . (A) C 1s, (B) N 1s, (C) O 1s, (D) Si 2p, (E) Zr 3d and (F) Au 4f.

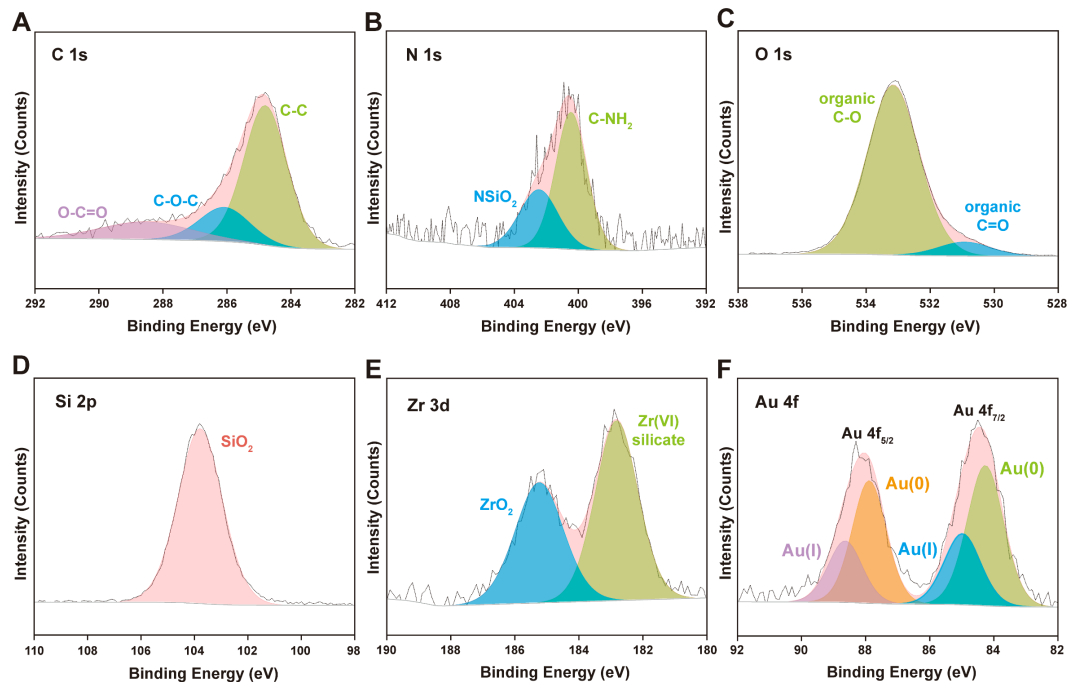


Figure S20. XPS spectrum of MSN@Zr@AgAu reacted with $\text{Cr}_2\text{O}_7^{2-}$. (A) C 1s, (B) N 1s, (C) O 1s, (D) Si 2p, (E) Zr 3d and (F) Au 4f.

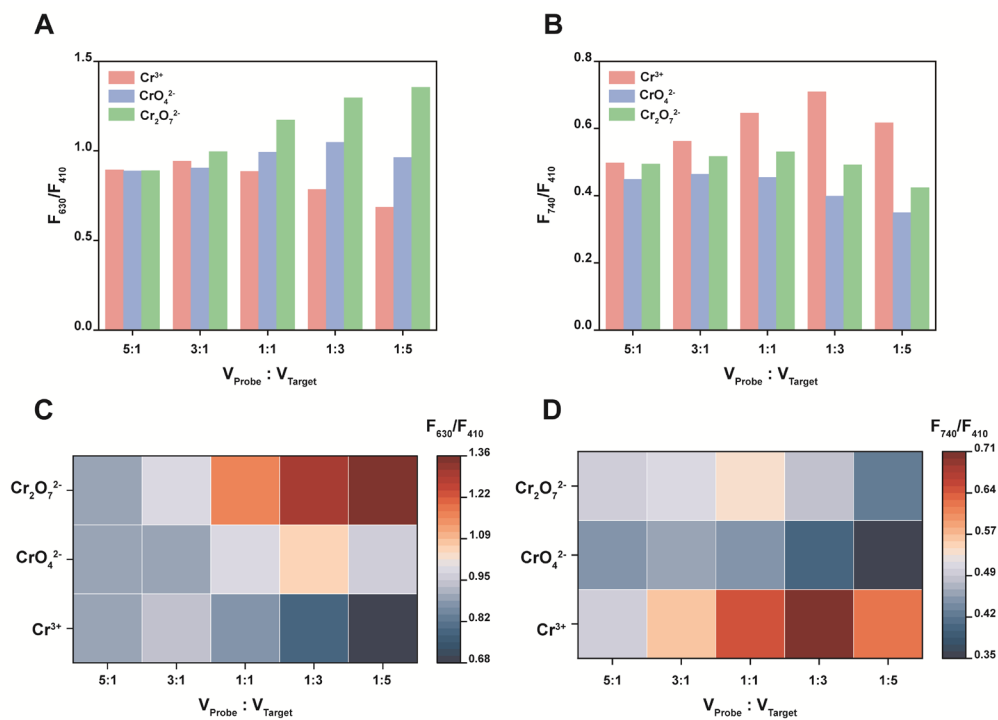


Figure S21. Optimization of volume ratio for the Cr detection based on MSN@Zr@Au NCs sensor array.

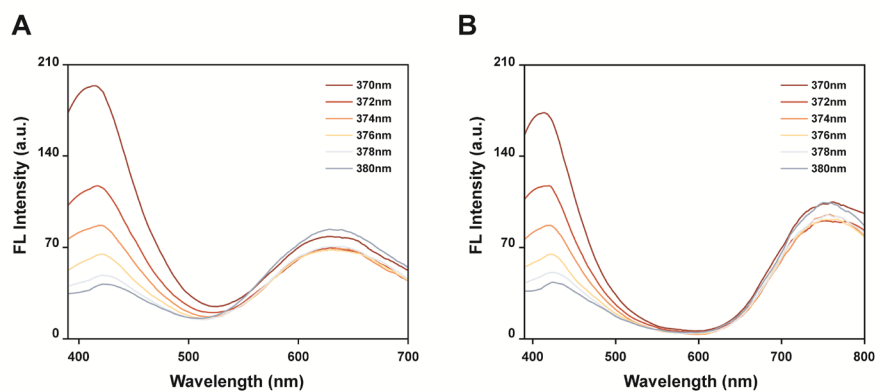


Figure S22. Fluorescence intensity of (A) MSN@Zr@Au and (B) MSN@Zr@AgAu at 370-380nm excitation.

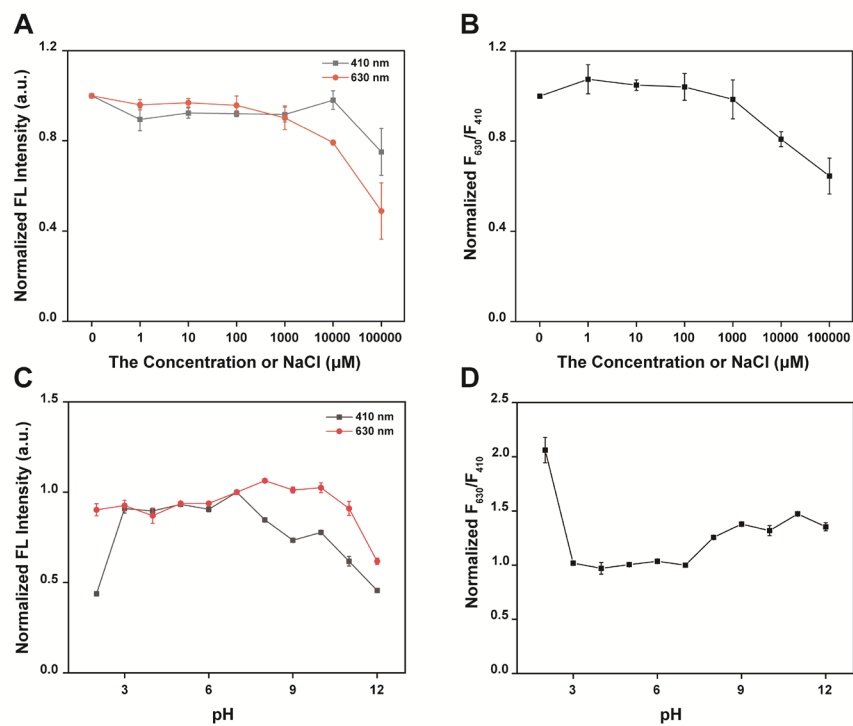


Figure S23. Optimization of ionic strength and pH based on MSN@Zr@Au.

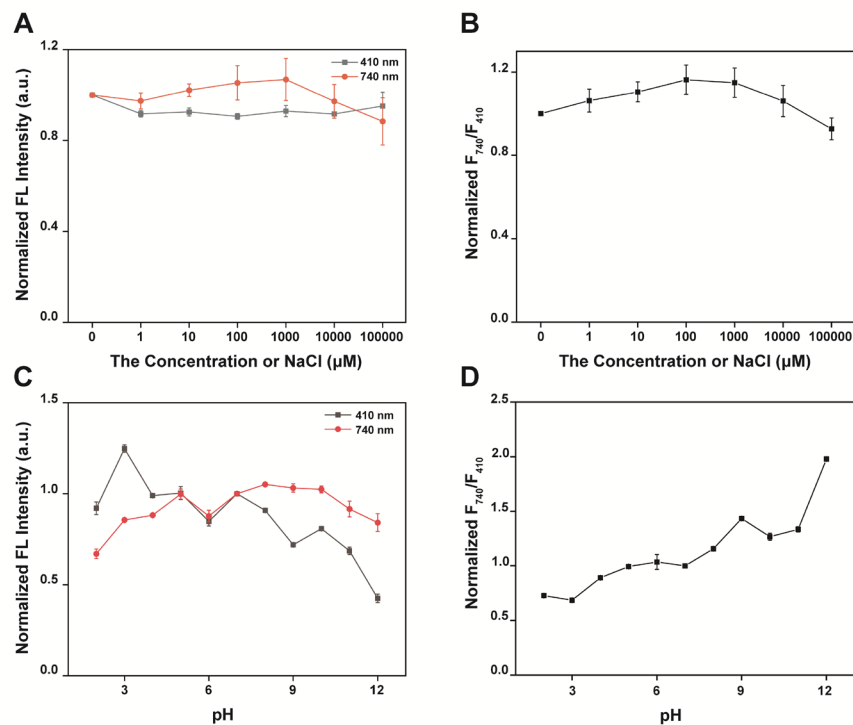


Figure S24. Optimization of ionic strength and pH based on MSN@Zr@AgAu.

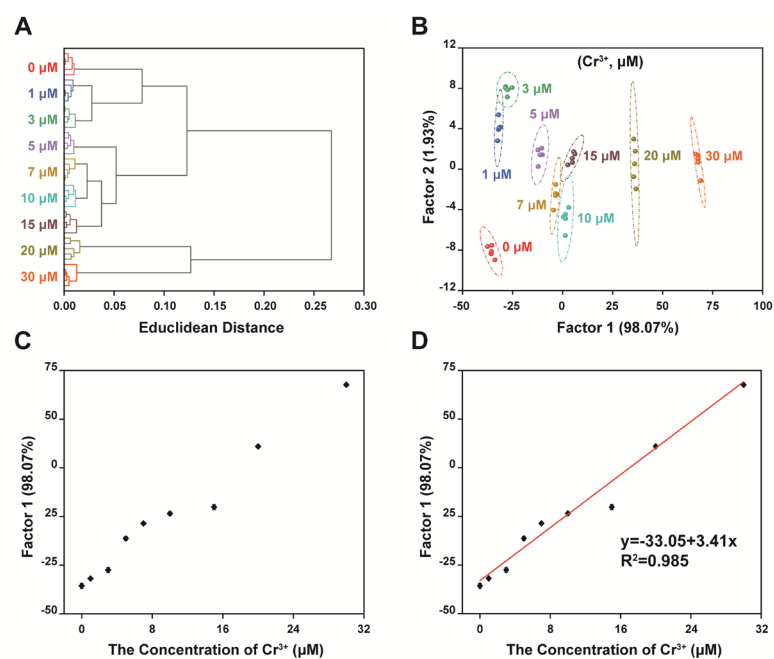


Figure S25. Quantitative detection of Cr^{3+} by sensor array. (A) HCA, (B) LDA, (C) scatter plot, and (D) Linear fitting curve.

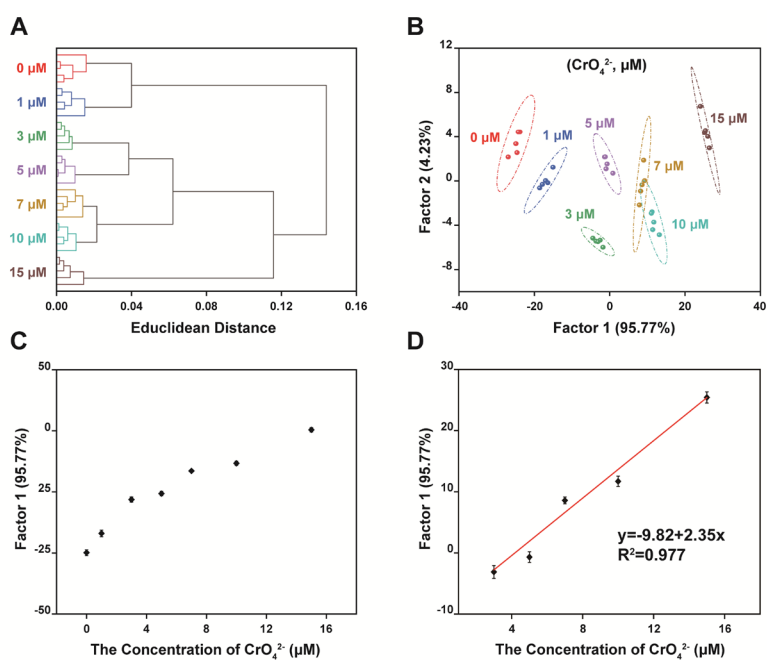


Figure S26. Quantitative detection of CrO_4^{2-} by sensors array. (A) HCA, (B) LDA, (C) scatter plot and (D) Linear fitting curve.

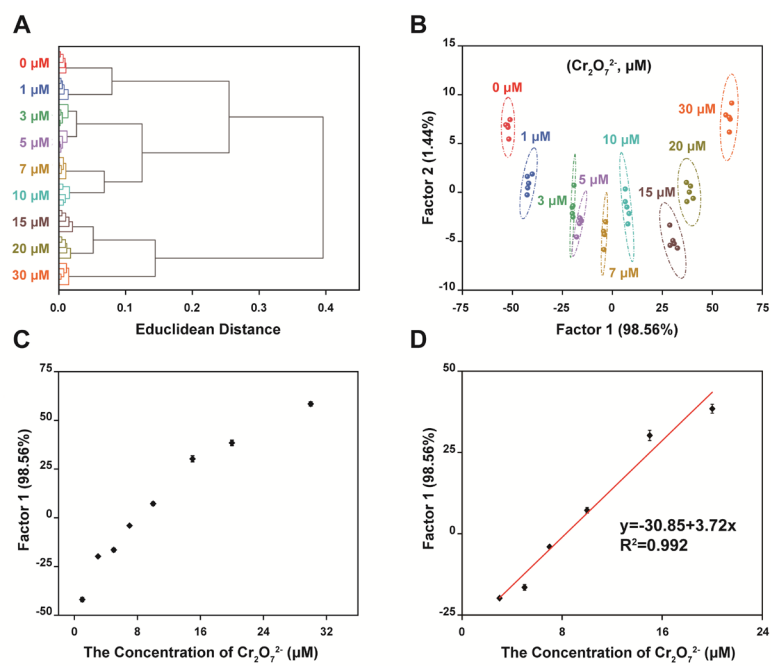


Figure S27. Quantitative detection of $\text{Cr}_2\text{O}_7^{2-}$ by sensors array. (A) HCA, (B) LDA, (C) scatter plot and (D) Linear fitting curve.

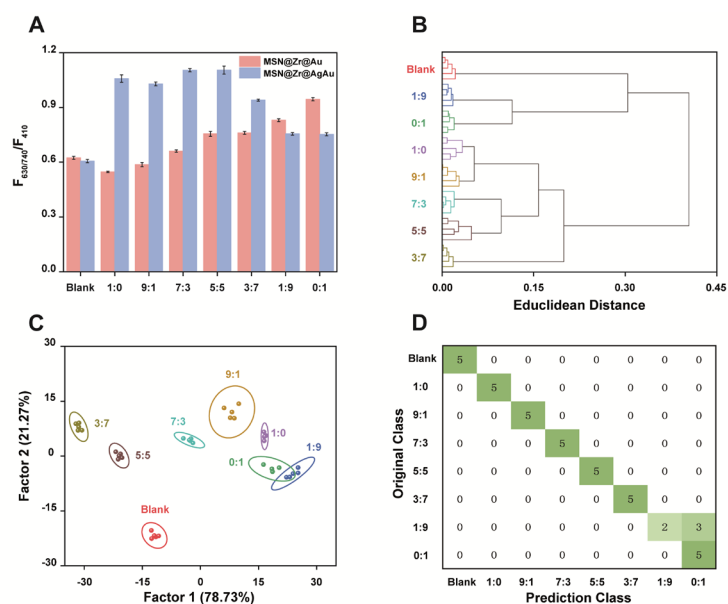


Figure S28. Discriminatory ability of the sensor array to identify $\text{Cr}^{3+} + \text{CrO}_4^{2-}$ at different molar ratio. (A) Fingerprint, (B) HCA plot, (C) LDA canonical score plot and (D) confusion matrix of the double-emission sensor array against $\text{Cr}^{3+} + \text{CrO}_4^{2-}$.

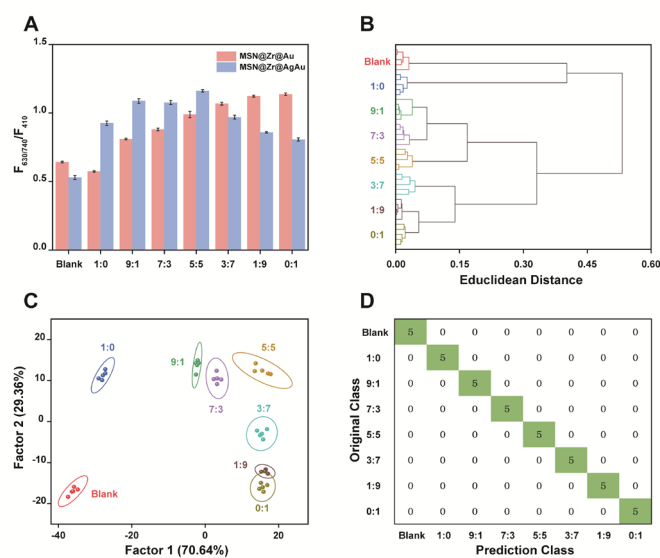


Figure S29. Discriminatory ability of the sensor array to identify $\text{Cr}^{3+} + \text{Cr}_2\text{O}_7^{2-}$ at different molar ratio. (A) Fingerprint, (B) HCA plot, (C) LDA canonical score plot and (D) confusion matrix of the double-emission sensor array against $\text{Cr}^{3+} + \text{Cr}_2\text{O}_7^{2-}$.

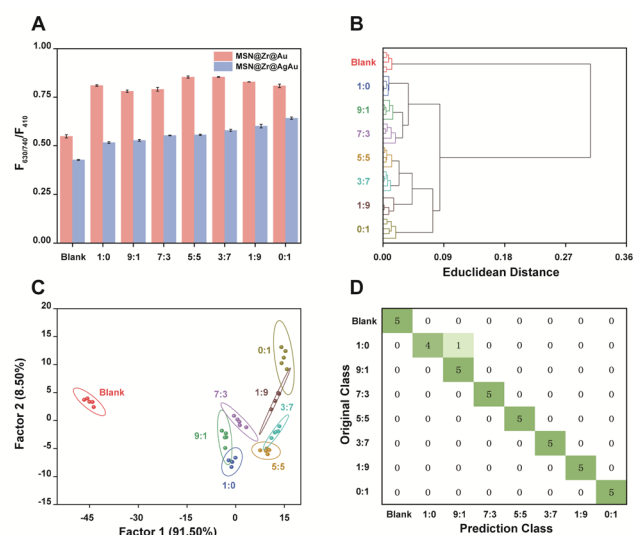


Figure S30. Discriminatory ability of the sensor array to identify $\text{CrO}_4^{2-} + \text{Cr}_2\text{O}_7^{2-}$ at different molar ratio. (A) Fingerprint, (B) HCA plot, (C) LDA canonical score plot and (D) confusion matrix of the double-emission sensor array against $\text{CrO}_4^{2-} + \text{Cr}_2\text{O}_7^{2-}$.

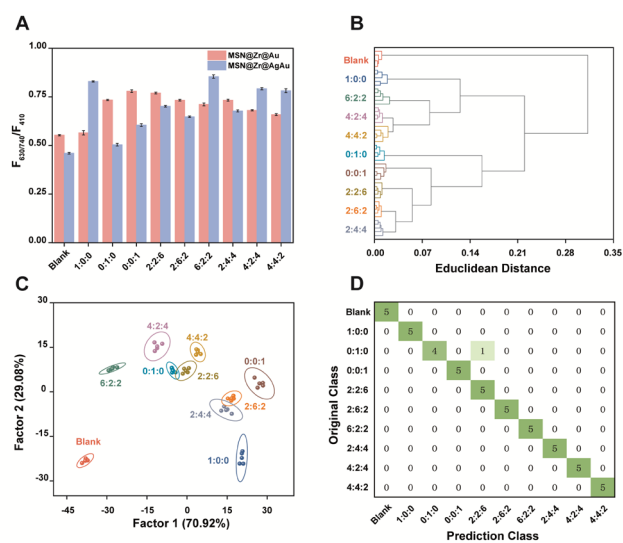


Figure S31. Discriminatory ability of the sensor array to identify $\text{Cr}^{3+} + \text{CrO}_4^{2-} + \text{Cr}_2\text{O}_7^{2-}$ at different molar ratio. (A) Fingerprint, (B) HCA plot, (C) LDA canonical score plot and (D) confusion matrix of the double-emission sensor array against $\text{Cr}^{3+} + \text{CrO}_4^{2-} + \text{Cr}_2\text{O}_7^{2-}$.

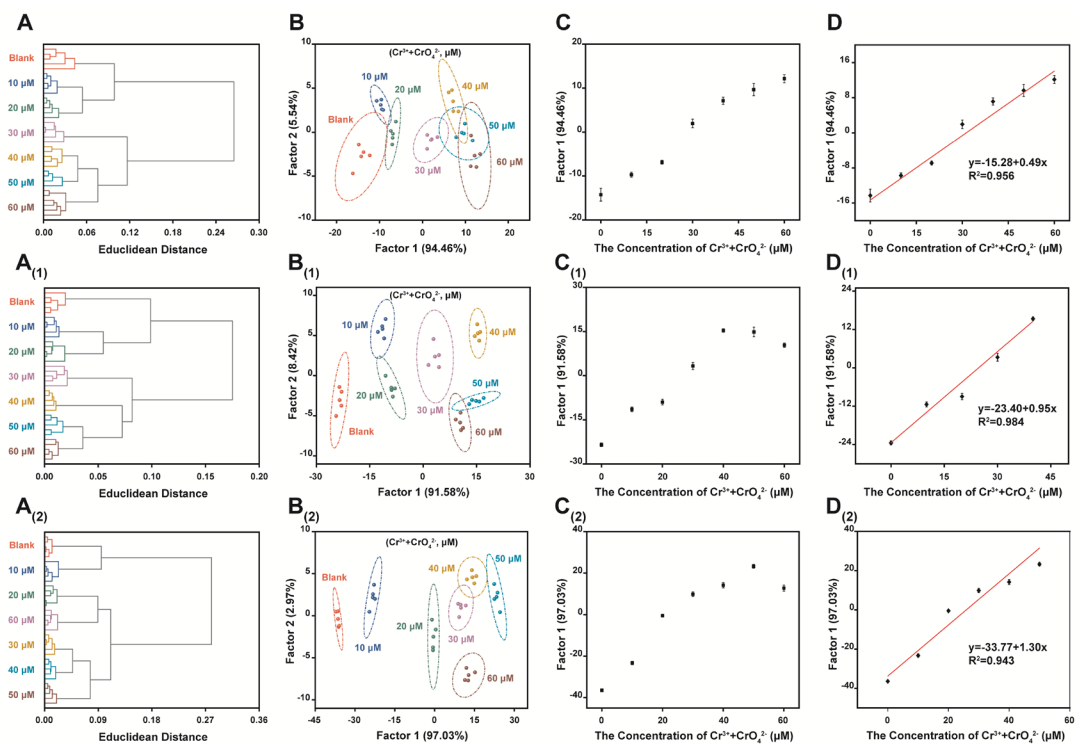


Figure S32. (A) HCA plot and (B) LDA canonical score plot for the discrimination of $\text{Cr}^{3+} + \text{CrO}_4^{2-}$ in different concentration (molar ratio is 1:1). (C) scatter plot and (D) Linear fitting curve of $\text{Cr}^{3+} + \text{CrO}_4^{2-}$ quantitative analysis (0-60 μM). The molar ratio of $\text{Cr}^{3+} : \text{CrO}_4^{2-}$ in (A₍₁₎-D₍₁₎) is 1:4; in (A₍₂₎-D₍₂₎) is 4:1.

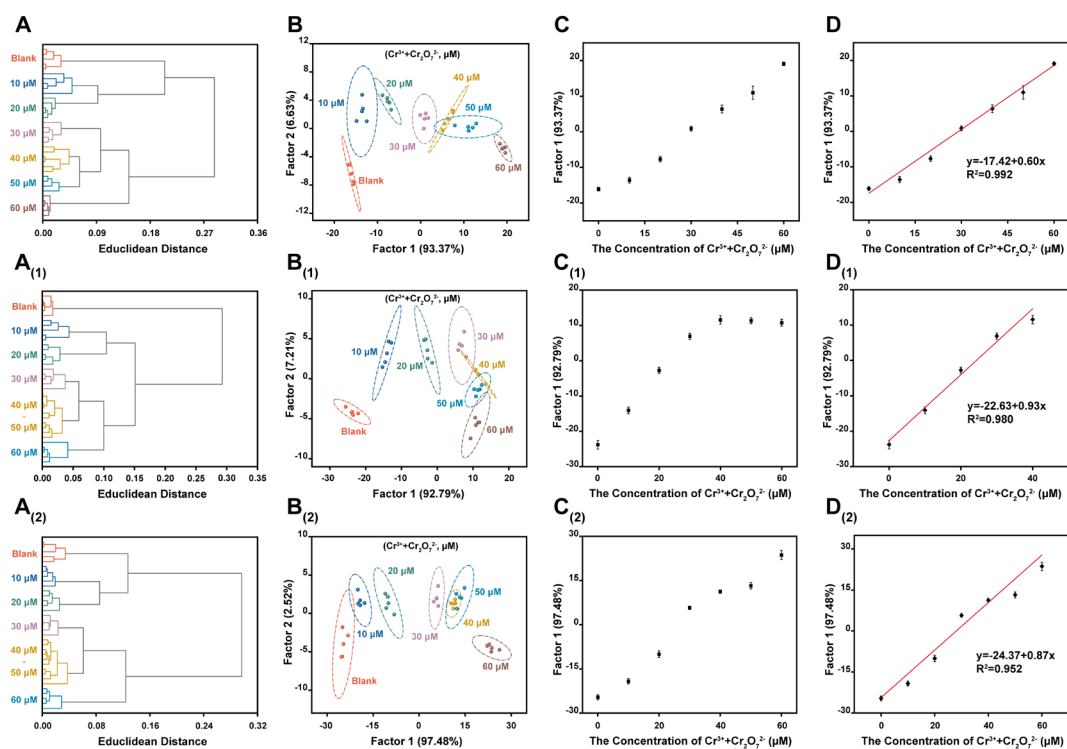


Figure S33. (A) HCA plot and (B) LDA canonical score plot for the discrimination of $\text{Cr}^{3+} + \text{Cr}_2\text{O}_7^{2-}$ in different concentrations (molar ratio is 1:1). (C) scatter plot and (D) linear fitting curve of $\text{Cr}^{3+} + \text{Cr}_2\text{O}_7^{2-}$ quantitative analysis (0-60 μM). The molar ratio of $\text{Cr}^{3+} : \text{Cr}_2\text{O}_7^{2-}$ in (A₍₁₎-D₍₁₎) is 1:4; in (A₍₂₎-D₍₂₎) is 4:1.

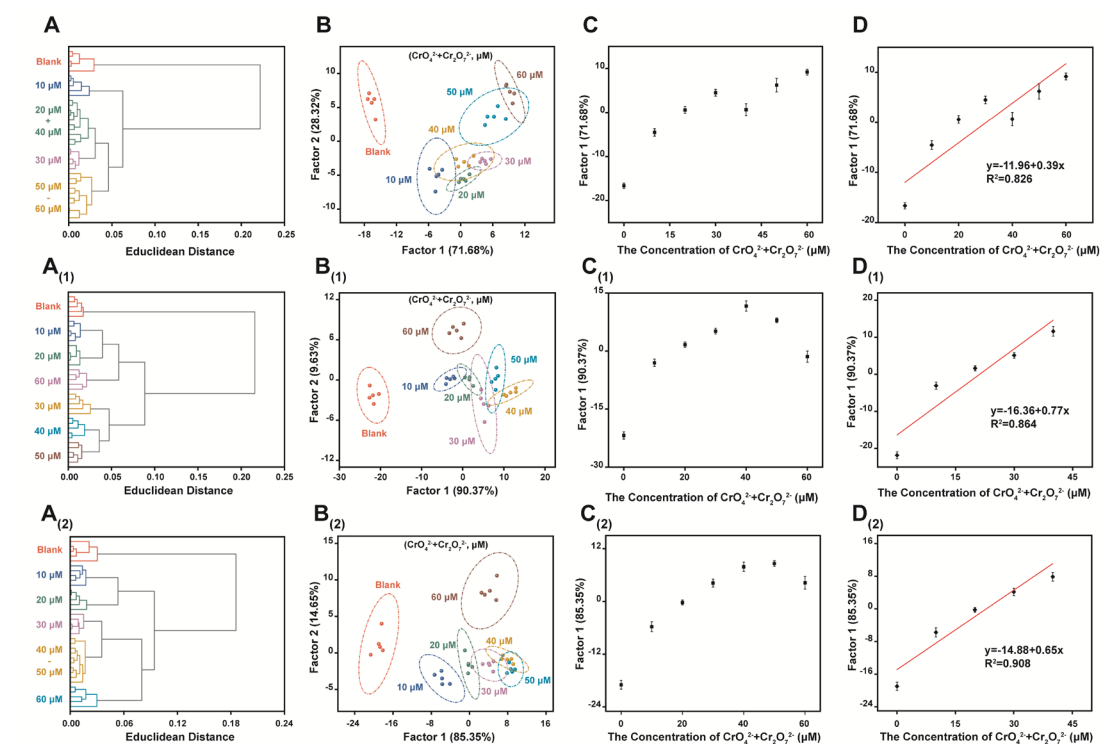


Figure S34. (A) HCA plot and (B) LDA canonical score plot for the discrimination of $\text{CrO}_4^{2-} + \text{Cr}_2\text{O}_7^{2-}$ in different concentration (molar ratio is 1:1). (C) scatter plot and (D) Linear fitting curve of $\text{CrO}_4^{2-} + \text{Cr}_2\text{O}_7^{2-}$ quantitative analysis (0-60 μM). The molar ratio of $\text{CrO}_4^{2-} : \text{Cr}_2\text{O}_7^{2-}$ in (A₍₁₎-D₍₁₎) is 1:4; in (A₍₂₎-D₍₂₎) is 4:1.

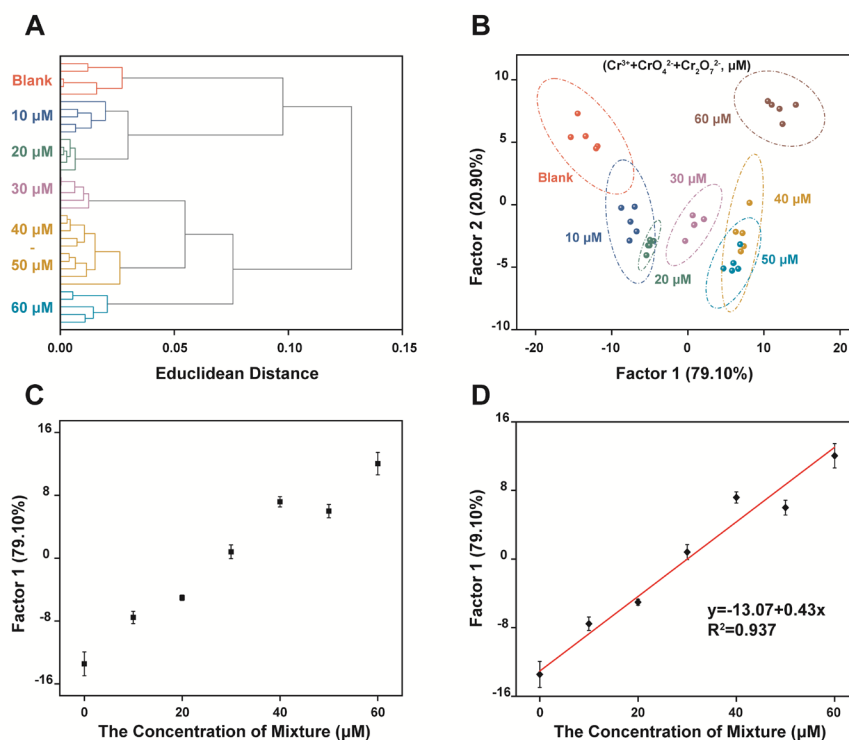


Figure S35. (A) HCA plot and (B) LDA canonical score plot for the discrimination of $\text{Cr}^{3+}+\text{CrO}_4^{2-}+\text{Cr}_2\text{O}_7^{2-}$ in different concentration (molar ratio is 1:1:1). (C) scatter plot and (D) Linear fitting curve of $\text{Cr}^{3+}+\text{CrO}_4^{2-}+\text{Cr}_2\text{O}_7^{2-}$ quantitative analysis (0-60 μM).

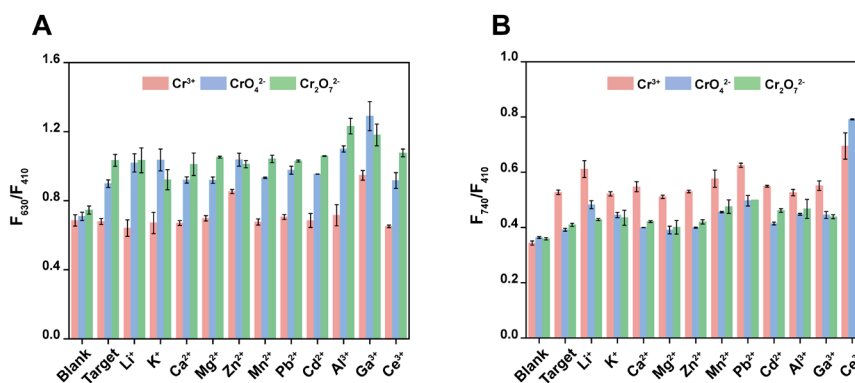


Figure S36. Anti-interference capability of sensor array. Effect of some interference ions of 150 μM (Li^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Mn^{2+} , Pb^{2+} , Cd^{2+} , Al^{3+} , Ga^{3+} , Ce^{3+}) on the Cr detection (all in 50 μM) by (A) MSN@Zr@Au and (B) MSN@Zr@AgAu.

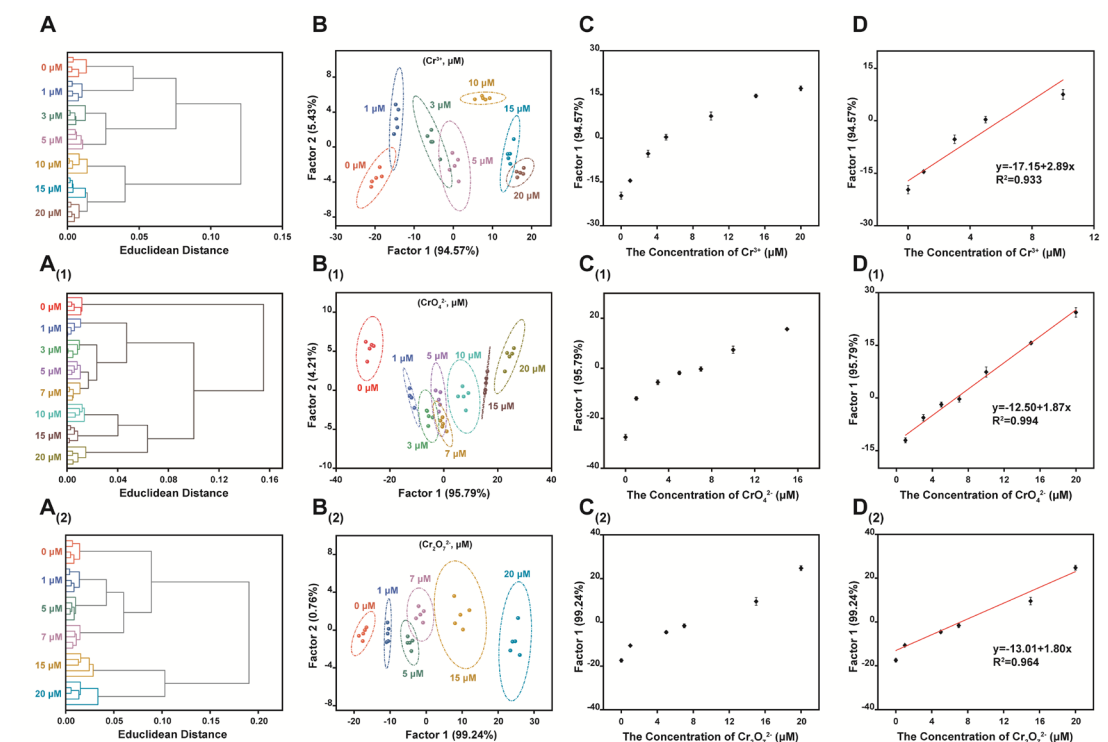


Figure S37. Quantitative ability of the sensor array to detect Cr^{3+} , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ in real samples. (A) HCA plot, (B) LDA canonical score plot, (C) scatter plot and (D) linear fitting curve of tap water spiked with Cr^{3+} . (A₍₁₎-D₍₁₎) and (A₍₂₎-D₍₂₎) are HCA plots, LDA canonical score plots, scatter plots and linear fitting curves of tap water spiked with CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ respectively.

Table S1. The quenching constant (K_{sv}) and quenching rate constant (K_q) of different Cr species

Emission	Constant	Cr^{3+}	CrO_4^{2-}	$\text{Cr}_2\text{O}_7^{2-}$
410 nm	K_{sv}	0.018 L/ μM	0.011 L/ μM	0.015 L/ μM
	K_q	1.1×10^{12} L/(M·s)	7.3×10^{11} L/(M·s)	9.9×10^{11} L/(M·s)
630 nm	K_{sv}	-	0.0044 L/ μM	0.017 L/ μM
	K_q	-	2.3×10^{11} L/(M·s)	8.9×10^{11} L/(M·s)
740 nm	K_{sv}	-	0.0037 L/ μM	0.011 L/ μM
	K_q	-	2.4×10^{11} L/(M·s)	7.3×10^{11} L/(M·s)

Table S2. Formulas for quantitative detection of Cr species at different molar ratios and concentrations by Factor 1 scores

Target	Equations	Range (μM)	R ²	LOD (μM)
Cr ³⁺	y=-33.05+3.41x	1-30	0.985	1.99
CrO ₄ ²⁻	y=-9.82+2.35x	1-15	0.977	3.28
Cr ₂ O ₇ ²⁻	y=-30.85+3.72x	1-20	0.992	1.29
Cr ³⁺ +CrO ₄ ²⁻ (1:1)	y=-15.28+0.49x	1-60	0.956	8.51
Cr ³⁺ +CrO ₄ ²⁻ (1:4)	y=-23.40+0.95x	1-40	0.984	5.63
Cr ³⁺ +CrO ₄ ²⁻ (4:1)	y=-33.77+1.30x	1-50	0.943	8.16
Cr ³⁺ +Cr ₂ O ₇ ²⁻ (1:1)	y=-17.42+0.60x	1-60	0.992	4.56
Cr ³⁺ +Cr ₂ O ₇ ²⁻ (1:4)	y=-22.63+0.93x	1-40	0.980	5.86
Cr ³⁺ +Cr ₂ O ₇ ²⁻ (4:1)	y=-24.37+0.87x	1-60	0.952	9.92
CrO ₄ ²⁻ +Cr ₂ O ₇ ²⁻ (1:1)	y=-11.96+0.39x	1-60	0.826	20.93
CrO ₄ ²⁻ +Cr ₂ O ₇ ²⁻ (1:4)	y=-16.36+0.77x	1-40	0.864	15.57
CrO ₄ ²⁻ +Cr ₂ O ₇ ²⁻ (4:1)	y=-14.88+0.65x	1-40	0.908	12.83
Cr ³⁺ +CrO ₄ ²⁻ +Cr ₂ O ₇ ²⁻ (1:1:1)	y=-13.07+0.43x	1-60	0.937	10.19

Table S3. The test Detection results of tap water by the proposed method

Sample	Metal ion	Spiked/ μM	Found/ μM	Recovery/%	RSD/%
Tap water		-	-	-	-
Sample 1	Cr^{3+}	8	9.0625	113.28	2.751
Sample 2		4	5.5520	138.80	4.860
Sample 3		16	15.1377	94.61	3.687
Sample 4	CrO_4^{2-}	8	8.5593	106.99	8.094
Sample 5		16	16.6561	104.10	4.993
Sample 6		8	7.6793	95.99	4.951

Table S4. The detection results of river water by the proposed method

Sample	Metal ion	Spiked/ μM	Found/ μM		Recovery/%	RSD/%
			ICP-MS			
			Sensor array			
River water		-	-		-	-
Sample 7	Cr^{3+}	8	8.2542	8.8745	110.93	4.477
Sample 8		4	4.3258	4.7589	118.97	6.911
Sample 9	CrO_4^{2-}	16	15.8756	16.1377	100.86	1.168
Sample 10		8	8.1252	7.7593	96.99	2.468
Sample 11	$\text{Cr}_2\text{O}_7^{2-}$	16	16.1251	16.9561	105.97	1.881
Sample 12		8	7.9855	8.6793	108.49	3.104

Table S5. Fluorescence lifetime of Hybridized fluorescent materials

Sample	Lifetime/ns	
	τ_1	τ_2
MSN@Zr@Au	2.63	19.01
MSN@Zr@Au +Cr ³⁺	3.27	15.40
MSN@Zr@Au +CrO ₄ ²⁻	2.53	15.51
MSN@Zr@Au +Cr ₂ O ₇ ²⁻	3.39	19.42
MSN@Zr@AgAu	2.71	15.02
MSN@Zr@AgAu +Cr ³⁺	2.72	15.94
MSN@Zr@AgAu +CrO ₄ ²⁻	3.12	13.88
MSN@Zr@AgAu +Cr ₂ O ₇ ²⁻	2.57	11.08

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