Ultrasensitive Photoelectrochemical Determination of Chromium (VI) in Water Samples by Ion-Imprinted/Formate Anion-Incorporated Graphitic Carbon Nitride Nanostructured Hybrid

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Graphical Abstract

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Abstract

A rapid and highly sensitive photoelectrochemical (PEC) method has been proposed for the determination of trace amounts of chromium in water samples under visible-light irradiation. Here, a unique nanostructured hybrid of formate anion incorporated graphitic carbon nitride (F-g-C₃N₄) is smartly integrated with a Cr(VI) ion-imprinted polymer (IIP) as a photoactive electrode (denoted as IIP@F-g-C₃N₄). The nanohybrid of F-g-C₃N₄ exhibits an enhanced charge separation with substantially improved PEC responses versus g-C₃N₄. The newly designed IIP@F-g-C₃N₄ PEC sensor exhibits high sensitivity and selectivity for the determination of Cr(VI) because it offers efficient photogenerated electron reduction toward Cr(VI). The PEC analysis is highly linear over Cr(VI) concentrations ranging from 0.01 to 100.00 ppb with a detection limit of 0.006 ppb ($S/N = 3$). Our approach can be used to detect Cr(VI), Cr(III) and the total chromium level in aqueous solution through oxidation of Cr(III) to Cr(VI) and the determination of the total chromium as Cr(VI). In practical applications, this low-cost and sensitive assay has been successfully applied for speciation determination of chromium in environmental water samples.

Keywords: Photoelectrochemical sensor; Ion imprinted polymer; Formate anion incorporated graphitic-carbon nitride; Hexavalent chromium

1. Introduction

Chromium ions are widely present in nature including water, soil, plants, and animals, but they are also a classic and dangerous contaminant [1]. Aqueous chromium exists

in two common and stable oxidation states: Cr(VI) and Cr(III). Cr(III) is an essential nutrient element for living organisms and is mostly harmless. In contrast, Cr(VI) is a carcinogen and is linked to carcinomas of the respiratory organs, mutations [2], chromosomal aberrations [3], and DNA damage [4]. World Health Organization guidelines limit Cr(VI) to 50 $\mu\text{g L}^{-1}$ in groundwater [5]. Measurements of trace levels of Cr(VI) as well as total chromium level in groundwater have attracted much attention for human health and environmental control. Generally, Cr(VI) is analyzed by atomic absorption spectroscopy, UV-vis spectroscopy, inductively coupled plasma-mass spectrometry, fluorescence, or electrochemical analysis [6–20]. However, these methods often suffer from some issues such as complicated separation/pre-concentration procedures, high cost, time-consuming, or lack of portability. Therefore, a simple, cheap and sensitive analytical method for fast pre-screening of Cr(VI) is urgently needed.

Recently, photoelectrochemical (PEC) sensors, a kind of sensing technique based on photoinduced electron transfer processes at electrode/interfaces, have received much interest [21–28]. They have remarkable sensitivity, portability, and easy integration. Photoactive materials-based PEC sensors such as nanostructured semiconductor materials [21–24], transition metal complexes [29–30], and conducting polymers [31], have been widely used in the various research areas. Nevertheless, few studies have been developed for the detection of chromium except for PEC sensing of Cr(VI) based on its selective inhibition of quercetin oxidation on a TiO_2 photoanode [21]. Obviously, developing a high-performance PEC sensing platform in a simple fashion

for the detection of chromium remains a significant challenge.

In recent years, metal-free polymeric graphitic-like carbon nitride ($\text{g-C}_3\text{N}_4$) has attracted worldwide research interests because of its specific electronic properties, low toxicity, low cost, high stability, and desirable band gap of 2.7 eV [32-34]. It has been explored for various applications in catalysis [35-36], degradation [37], and, lately, as sensing probes [38-41]. The conduction band (CB) and valence band (VB) potentials of $\text{g-C}_3\text{N}_4$ were reported to be -1.3 and 1.4 V versus NHE, respectively. The more negative conduction band potential of $\text{g-C}_3\text{N}_4$ than the reduction potential of Cr(VI)/Cr(III) (1.33 V versus NHE) enables $\text{g-C}_3\text{N}_4$ to reduce Cr(VI) into Cr(III) under visible-light irradiation [34]. This provides the feasibility to establish a $\text{g-C}_3\text{N}_4$ -based PEC sensing platform for detection of Cr(VI) . Nevertheless, pure $\text{g-C}_3\text{N}_4$ suffers from low photoreactivity resulting from the fast recombination of photogenerated electron-hole pairs. Thus, coupling $\text{g-C}_3\text{N}_4$ with foreign elements has become an effective strategy to improve the photoreactivity of pure $\text{g-C}_3\text{N}_4$ [42-45]. Recently, our group successfully synthesized $\text{g-C}_3\text{N}_4$ nanohybrid incorporating formate anions, which are a typical hole scavenger; this was labeled as $\text{F-g-C}_3\text{N}_4$ [45]. It has been demonstrated that the photoreduction ability of $\text{g-C}_3\text{N}_4$ could be significantly enhanced with photogenerated holes trapped by incorporated formate anions. This greatly improves the photoactivity of $\text{g-C}_3\text{N}_4$. Inspired by this, we present here for the first time the use of $\text{F-g-C}_3\text{N}_4$ nanohybrids integrated with molecularly-imprinted polymers (MIPs) as a PEC sensing platform for the determination of Cr(VI) . The smart integration of $\text{F-g-C}_3\text{N}_4$ and Cr(VI) ion-imprinted

poly(4-vinyl pyridine-co-hydroxyethyl methacrylate) (labeled as IIP) yields a novel IIP@F-g-C₃N₄ hybrid-based photoactive electrode for the determination of Cr(VI). After oxidation of Cr(III) by H₂O₂, the system could also be used to quantify the amount of Cr(III) and total chromium. The application of the as-prepared IIP@F-g-C₃N₄ PEC sensing probe for speciation determination of chromium in nature water samples was studied in detail. To the best of our knowledge, this is the first report on the use of visible-light-responsive IIP functionalized F-g-C₃N₄ for PEC speciation analysis of chromium species in water samples.

2. Experimental section

2.1 Chemicals and materials

All chemicals used in this work were of analytical grade and were used without further purification. Melamine and potassium dichromate (K₂Cr₂O₇) were purchased from Sinopharm Chemical Reagent Co. Ethyleneglycol dimethacrylate (EGDMA) and α - α '-azoisobutyronitrile (AIBN) were purchased from Shanghai chemical Corporation of China. The 2-hydroxyethyl methacrylate (HEMA) was purchased from Tianjin Chemical Reagent Research Institute Co, and 4-vinyl pyridine (4-VP) and poly dimethyl diallyl ammonium chloride (PDDA) were obtained from Aladdin Industrial Co., respectively. The buffer solutions of 0.1 M Tris (hydroxymethyl) aminomethane hydrochloride (Tris-HCl) with different pH values were prepared for use. The FTO (fluorine-doped tin oxide glass) was purchased from NSG, Japan. Ultrapure water (resistivity ≥ 18 M Ω) was used, and all experiments were carried out at room temperature.

2.2 Apparatus

Electrochemical and PEC measurements were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) with a conventional three electrode system comprising a platinum wire as the auxiliary electrode, a saturated calomel electrode (SCE) as the reference electrode, and the as-prepared ion imprinted F-g-C₃N₄ or non-ion imprinted F-g-C₃N₄ onto FTO electrode as the working electrode. Electrochemical impedance spectra (EIS) were measured in the frequency range from 0.1 Hz ~ 100 kHz with a signal amplitude of 5 mV at CHI 660D. During the electrochemical measurements, the surface area of the working electrode was 3.0 cm². A 500W Xe lamp (Shanghai LanSheng Electronic Co., China) equipped with a monochromator was used as the irradiation source ($\lambda = 420$ nm). Powder X-ray diffraction (XRD) measurements of all samples were collected using a Rigaku Ultima III X-ray diffractometer with high-intensity Cu K α_1 irradiation ($\lambda = 1.5406$ nm). UV-vis diffuse reflectance spectra were collected on an UV-vis spectrometer (Shimadzu UV-2550). Fluorescent emission spectra were recorded on a RF-5301PC spectrofluorometer (Shimadzu, Japan). An inductively coupled plasma mass spectrometer (ICPMS, ThermoFisher X series II, USA) was used for the measurements of Cr species.

2.3 Synthesis of g-C₃N₄ and formate anion incorporated g-C₃N₄ (F-g-C₃N₄)

Pure g-C₃N₄ powders were prepared by directly heating melamine at 520 °C for 4 h. The sample of formate-anion incorporated g-C₃N₄ (F-g-C₃N₄) was synthesized by hydrothermal treatment of the as-prepared g-C₃N₄ [45]. Typically, 0.01g of sodium

formate and 0.5g of g-C₃N₄ were placed in a 100 mL Teflon-lined stainless steel autoclave with distilled water at 80% of the total volume. The autoclave was then sealed and heated at 150 °C for 24 h. The resulting powder was collected by filtration, washed with ethanol thoroughly, and finally dried in an oven at 50 °C.

2.4 Preparation of Cr(VI) ion-imprinted polymers (IIPs)

The IIP was prepared according to the reported methods [46]. 4-vinylpyridine (4-VP), EGDMA, and AIBN were used as the functional monomer, crosslinker and initiator agent of the imprinted polymerization, respectively. Briefly, 3 mL 4-VP and 0.8826 g K₂Cr₂O₇ were treated with methanol/acetonitrile (50 mL, V/V = 1:1) for 1 h at room temperature to form a metal–monomer complex of 4-VP-Cr(VI). Next, the product was slowly dropped into a mixture of 17 mL 2-HEMA and 10 mL EGDMA containing 1.5 g AIBN. The resulting polymerization mixture was equilibrated in a water bath at 25 °C for 15 min and purged with nitrogen for 10 min. Subsequently, the polymerization was carried out under a long-wave UV radiation for 2 h followed by centrifugation to collect the ion-imprinted polymer. The grained imprinted particles were extensively washed with an ethanol/water mixture (70/30, V/V) for 6 h at room temperature to remove unreacted monomers and other ingredients. After cleaning, the template metal ions were removed with acidified thiourea solution (0.5% thiourea in 0.5 M HCl) for 24 h at 25 °C under magnetic stirring (labeled as IIP). For comparison, non-imprinted polymers were prepared similarly without Cr(VI) templates during polymerization; these were labeled NIP.

2.5 Design and fabrication of chromium PEC sensor

Prior to the preparation of the modified photoactive electrodes, the basal FTO substrates were cleaned with ultrasonication in distilled water and ethanol, respectively. The as-prepared F-g-C₃N₄ powder was dispersed into PDDA (4 mg L⁻¹) aqueous solution. Here, the introduced PDDA could not only improve the dispersion of F-g-C₃N₄, but also act as an immobilization matrix of F-g-C₃N₄ via electrostatic interaction between positive PDDA and negative F-g-C₃N₄. Then, 100 μ L of a 5.0 mg mL⁻¹ F-g-C₃N₄ dispersion was dropped onto the surface of the cleaned FTO and was kept at room temperature until dry (labeled as F-g-C₃N₄/FTO). Afterwards, an optimized amount of IIP dispersion (20 μ L, 0.5 mg mL⁻¹) was cast onto the surface of F-g-C₃N₄/FTO and dried at room temperature to obtain an electrode of IIP@F-g-C₃N₄/FTO. As a control, NIP on F-g-C₃N₄/FTO was also prepared (NIP@F-g-C₃N₄/FTO) under the same conditions without using template molecules.

2.6 PEC measurements

All PEC measurements were performed using a conventional three-electrode system in a quartz cell. Photocurrents were recorded in 0.1 M Tris-HCl (pH = 6.0) before and after the incubation of IIP@F-g-C₃N₄/FTO into different concentrations of Cr(VI) solutions for 10 min, respectively.

3. Results and discussion

3.1 Characterization studies

The phase structure of the as-prepared g-C₃N₄ and F-g-C₃N₄ was studied by XRD patterns (Fig. 1A). Both of them exhibit two peaks near 13.0 and 27.4°, corresponding

to (100) and (002) crystal planes of g-C₃N₄ (curve a) (JCPDS 87-1526). No impurities can be detected in F-g-C₃N₄, indicating that the incorporation of formate anions does not change the phase structure of g-C₃N₄. The peak at 27.4° in the XRD pattern of F-g-C₃N₄ corresponds to the characteristic interlayer stacking reflection of conjugated aromatic systems as an (002) peak. It became weaker and shifted toward a higher 2θ value. This shift suggests a successful inclusion of formate anions in g-C₃N₄, with the incorporated formate anions located in the in-plane holes of carbon nitride (bound to the nitrogen atoms) [45, 47]. Fig. 1B displays the photoluminescence (PL) spectra of g-C₃N₄ and F-g-C₃N₄ under 330-nm excitation. The strong emission peak at around 440 nm is derived from the direct electron/hole recombination of band transition [48-49]. The weaker PL intensity of F-g-C₃N₄ undoubtedly confirms that the inclusion with formate anions could greatly suppress the recombination of photogenerated charge carriers. The photocurrent responses of F-g-C₃N₄/FTO, g-C₃N₄/FTO, and bare FTO electrodes under visible-light illumination were further explored (Fig. 1C). The g-C₃N₄/FTO electrode shows a stable photocurrent of 78.5 nA (curve b), whereas the PEC responses of the F-g-C₃N₄/FTO electrode exhibit substantial improvement. This suggests a notably enhanced charge separation at formate incorporated g-C₃N₄ (curve c), which agrees well with the PL results.

The capability of electron transfer of different electrodes was investigated by electrochemical impedance spectra (EIS) (Fig. 1D). The EIS of the bare FTO is composed of a semicircle and a straight line featuring a diffusion-limiting step of the Fe(CN)₆^{4-/3-} (curve a). With the formation of F-g-C₃N₄ on the FTO, the semicircle

increases significantly, suggesting the hindrance effects of the semiconductor F-g-C₃N₄ film on the interfacial charge transfer (curve b). After further modification of Cr(VI) ion-imprinted IIP onto F-g-C₃N₄/FTO, the semicircles distinctively increase. Obviously, the nonconductive properties of IIPs obstruct the electron transfer and mass transport of the electrochemical probe resulting in the increased resistance (curve c). Interestingly, after removal of Cr(VI), the impedance decreased (curve d). Removal of Cr ions left a lot of cavities in IIP, and thus reduced the mass-transfer resistance of [Fe(CN)₆]^{3-/4-} through the IIP film, indicating the successful preparation of IIP-modified F-g-C₃N₄.

The FTIR spectra were measured to get direct evidence for the complex formation between Cr(VI) anions and 4-VP groups of the IIP (Fig. 2). The broad band from 3300 to 3500 cm⁻¹ indicates -OH stretching vibrations in the structure of the acrylic polymers (i.e., HEMA and EGDMA) [47]. Two peaks at ~ 2959 and 1729 cm⁻¹ correspond to the characteristic absorption peaks of ethylene vibration and ester configurations in HEMA/EGDMA, respectively. With the entrapment of Cr(VI) by IIP (curve b), there is a characteristic absorption band at 2351 cm⁻¹ representing the vibration of aromatic rings (i.e. 4-VP) complexed with Cr(VI) anions. Another new band was observed at 1559 cm⁻¹, which could be assigned to the characteristic stretching vibration of the pyridine group after complexation of Cr(VI) anions. These results further confirm the successful synthesis of Cr(VI)-IIPs via the complexation.

3.2 Optimization of detection conditions

To get high-performance visible-light-activated PEC responses of IIP@F-g-C₃N₄/FTO,

several optimized experiments were carried out. The effect of the amount of F-g-C₃N₄ on the PEC responses was first observed. The photocurrent initially rises with the concentration of the F-g-C₃N₄ dispersion up to 5 mg L⁻¹ and then decreases (Fig. 3A). This is likely related to the nanostructured platform of F-g-C₃N₄ on the electrode. As the amount of F-g-C₃N₄ further increased, some aggregated nanostructures were produced, resulting in the decreased PEC performance. **The thicker F-g-C₃N₄ film may hinder electron transfer from the outside layer of the F-g-C₃N₄ to the electrode.** Thus, the optimal dispersion concentration of F-g-C₃N₄ is 5 mg L⁻¹.

As the recognition element, the amount of IIP dispersed onto the F-g-C₃N₄/FTO sharply influenced the PEC response of Cr(VI). **The final PEC response of Cr(VI) at IIP@F-g-C₃N₄/FTO first increased up to 20 μ L as a function of different volumes of IIP dispersion (0.5 mg L⁻¹) onto F-g-C₃N₄/FTO, and then decreased at higher amounts** (Fig. 3B). Incubation time is another influential parameter in PEC analysis. With increasing incubation time in the Cr(VI) solution, the photocurrent on IIP@F-g-C₃N₄/FTO increased rapidly during the initial time for 10 min and then became stable (Fig. 3C). When the immersion time was longer than 10 min, the binding interactions (recognition process) reached saturation. Thus, the optimum incubation time is 10 min for the PEC determination of Cr(VI).

The PEC responses of IIP@F-g-C₃N₄/FTO also depend on the pH. Curve a (in Fig. 3D) shows the variations in photocurrent at IIP@F-g-C₃N₄/FTO with pH. The photocurrent of IIP@F-g-C₃N₄/FTO decreased with pH values from 2.0 to 6.0 and then leveled off at a high pH value of 6.5-8.0 (curve a). At lower pH values, it is

easier for the protons to capture the photogenerated electron of F-g-C₃N₄. This led to the enhanced photocurrent. After immersion in 1 µg L⁻¹ Cr(VI) solution, the photocurrents were increased dramatically within the observed pH value of 2.0-8.0 (curve b). The change in photocurrent indicates that the photocurrent increase is especially obvious at lower pH values of 2.0-5.0. It remained stable at pH 5.0-6.5 and finally dropped off at high pH values of 7.0-8.0 (curve c). This could be attributed to the higher oxidation ability of Cr(VI) in acidic solution and the efficient photoreduction of Cr(VI) by photogenerated electrons over F-g-C₃N₄. Thus, considering the real applications, mild pH 6.0 conditions were used in the detection solution.

3.3 Analytical performance for the detection of Cr (VI)

Under optimized experimental conditions, the photocurrents of modified FTO electrode in 0.1 M Tris-HCl (pH = 6) buffer solution containing different concentrations of Cr(VI) were recorded (shown in Fig. 4A). With increasing concentrations of Cr(VI) in the immersion solution, the produced photocurrent of IIP@F-g-C₃N₄/FTO increased successively. Owing to the redox potential of Cr(VI)/Cr(III) (1.33 V versus NHE) lying between the conduction (− 1.3 V) and the valence bands (1.4 V) of F-g-C₃N₄, it allows the efficient photoreduction of Cr(VI) to Cr(III) by photogenerated electrons over F-g-C₃N₄ [34]. Meanwhile, the incorporated formate anions could effectively trap photogenerated holes. As a result, the charge transfer would effectively suppress the electron-hole pair recombination and prompt the separation of the photogenerated carriers, thus leading to the increased

photocurrent (as illustrated in Scheme 1). The relative change in the photocurrent ($\Delta i/i_0$, Δi equals $i - i_0$, where i_0 and i is the photocurrent before and after incubation in Cr(VI)) is linearly proportional to the logarithm value of Cr(VI) concentrations in the range of 0.01 to 100.00 $\mu\text{g L}^{-1}$, with a correlation coefficient of $R = 0.9948$ (shown in Fig. 4B). The detection limit (S/N=3) is estimated to be 0.006 $\mu\text{g L}^{-1}$ (i.e. 6 ppt) based on the response of three times the standard deviation of the zero-dose response ($n = 6$). This detection limit is significantly lower than those of FAAS (~ 0.8 ppb) [50], ICP-MS (~ 10.0 ppb) [51], and electrocatalytic detection (~ 5.2 ppb) [20]. It is also superior to that of fluorescence technique [14]. According to the US Environmental Protection Agency standard, the maximum acceptable total Cr concentration in drinking water should be less than 100 ppb (1.9 μM). Thus, the proposed approach is sensitive enough to monitor Cr(VI) levels in drinking water. Moreover, the cost of the PEC sensor is markedly reduced because it is simpler and uses more common instruments. This makes it suitable for in situ measurements of Cr(VI) in real samples.

3.4 Selectivity

To investigate the selectivity of the as-prepared PEC sensor towards Cr (VI), the effects of other potentially interfering metal ions on the photocurrent intensity of the IIP@F-g-C₃N₄/FTO electrodes were examined. Fig. 5 shows the response of the PEC sensor toward 10 $\mu\text{g L}^{-1}$ of each compound. The photocurrent of IIP@F-g-C₃N₄/FTO shows negligible change upon immersion into the solution of non-specific ions. There is less than 3.0% photocurrent change except for Cu(II) and Fe(III). The electron transfer between Cu(II) or Fe(III) and IIP@F-g-C₃N₄/FTO is more favorable because

of the more positive redox potential of Cu(II) and Fe(III) versus other metal ions. The normalized photocurrent change is 90.0, 29.5, and 9.35% for Cr(VI), Cu(II), and Fe(III), respectively. To exclude such interferences, EDTA was added to the immersion solution as an efficient masking reagent. The interference from Cu(II) and Fe(III) could be notably reduced. Further addition of $10\ \mu\text{g L}^{-1}$ Cr(VI) into the above solution tested the selectivity of the PEC sensor in a two-component system. Compared to the PEC response of Cr(VI) alone, the photocurrent of IIP@F-g-C₃N₄/FTO exhibits negligible change in the two-component system containing $10\ \mu\text{g L}^{-1}$ Cr(VI) and equal concentrations of individual interference. Even when the concentration of the interfering metal ions is 20 times that of Cr(VI), one can see that all the photocurrent deviations are less than 9.8%. These data show that this IIP@F-g-C₃N₄/FTO photoelectrode presents high selectivity.

The imprinting factor (S) is an important parameter in evaluating the effectiveness of the imprinting process. It expresses the ratio of the photocurrent of target under specific-to-nonspecific binding ($S = \Delta i_{\text{MIP}}/\Delta i_{\text{NIP}}$). The value of Δi equals $i - i_0$, where i_0 and i are the photocurrent in Tris-HCl before and after addition of targets, respectively. The S value is used to further investigate the selectivity of this PEC sensor. During the experiments, the photocurrents with different single components of $100\ \mu\text{g L}^{-1}$ Cr(VI), Cr(III), Cu(II), Co(II), Pb(II), Fe(III), Zn(II), Ni(II) and Cd(II) were recorded, respectively (See Fig. S1). The highest S value of 5.86 was obtained for Cr(VI) (Table S1), further demonstrating the outstanding selectivity of this PEC sensor. Evidently, the superior selectivity toward the detection of Cr(VI) can be mainly due to shape

identification, the complex interaction from IIP, and the higher oxidation ability of Cr(VI) under acidic solution.

3.5 Reproducibility and stability of the PEC sensor

To investigate the reproducibility of the as-fabricated sensor, intra-assay and inter-assay measurements were performed. The intra-assay RSD is 2.65% for five replicate measurements of 100 $\mu\text{g L}^{-1}$ Cr(VI), and the inter-assay RSD is 3.80% for five independent PEC sensors measuring 100 $\mu\text{g L}^{-1}$ Cr(VI). These data suggest acceptable reproducibility. Operational stability is also a major concern for practical applications. There was no obvious decrease in the response of Cr(VI) in the first 10-day storage. After 30 days of storage, the sensor retained 96% of its initial current response, demonstrating a good stability of the PEC sensor.

3.6 Analysis of environmental water samples for the speciation determination of Cr

To further demonstrate the practicality of this electrode, the proposed PEC sensor was then applied to the speciation determination of Cr(III) and Cr(VI) in natural water samples including tap and river water samples. River water samples were collected from the Yangtze River (Wuhan, China) and East Lake (Wuhan, China), respectively. To determine the content of hexavalent chromium, water samples (500 mL) were treated with 2.5 mL 65% HNO_3 and boiled for 20 min to remove some coexisting organic substances. The pH value of the residual sample was adjusted to 9.0 with ammonia and warmed for ~20 min to precipitate some potential metal ions (including Fe^{3+} , Cu^{2+} contents). Then water samples were filtered and adjusted to pH 6.0 before Cr(VI) measurements with the PEC method. To determine the total chromium content,

1 mL 30% H₂O₂ was added to the water samples before adjusting the pH value to 9.0 to oxidize Cr(III) ions to Cr(VI). The process was then continued according to the above discussion. Under such conditions, the Cr(III) content was obtained by subtracting Cr(VI) from the total chromium content. Table 1 shows that the recoveries obtained for the spiked amounts are 89.8% to 109.4%. The original trace amount of total chromium in the river water samples was 0.365 (tap water), 0.763 (Yangtze River) and 0.205 ppb (East Lake), respectively. The accuracy of the method was also assessed by comparing the PEC results to those obtained by ICP-MS. The ICP-MS values were 0.388 ± 0.002 ppb (tap water), 0.716 ± 0.003 ppb (Yangtze River), and 0.215 ± 0.002 ppb (East Lake), respectively, showing difference all less than 6.5%. The results indicated that the proposed method is highly accurate, precise, and reproducible. It can be used for direct analysis of relevant samples. Most importantly, PEC sensor is simple, rapid, and cheap relative to ICP-MS.

4. Conclusion

In summary, we developed a new PEC approach for the real-time detection of Cr(VI) without interference from a wide range of other metal ions, and further exploited its application on the speciation determination of chromium. The first smart integration of nanoarchitected F-g-C₃N₄ with IIP offers a high-performance photoactive sensing platform. The resulting sensor is highly sensitive, specific, and selective. We believe that this study provides a promising PEC strategy for real world analysis of environmental and food samples.

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Figure Captions

Scheme 1. Schematic illustration of the formation process of (A) the IIP, and (B) the principle of PEC determination of Cr(VI) using IIP@F-g-C₃N₄/FTO.

Table 1. PEC speciation determination of Cr(VI) and Cr(III) in different water samples using the proposed method ($n=3$).

Figure 1. (A) XRD patterns of the as-prepared (a) bulk g-C₃N₄ and (b) F-g-C₃N₄; (B) PL spectrum of (a) g-C₃N₄ and (b) F-g-C₃N₄ solid powder when excited at 365 nm; (C) Photocurrent responses of (a) bare FTO, (b) g-C₃N₄/FTO, (c) F-g-C₃N₄/FTO with on-off illumination under visible light. The supporting electrolyte was 0.1 M pH 6.0 Tris-HCl; (D) Electrochemical impedance spectra of (a) FTO foil, (b) F-g-C₃N₄/FTO, and IIP@F-g-C₃N₄/FTO before (c) and after (d) removal of Cr(VI) in 0.1 M PBS containing 2.5 mM K₃[Fe(CN)₆]/K₄[Fe(CN)₆] (1:1). The applied frequency was 0.1 Hz to 100 kHz.

Figure 2. FTIR spectra of the as-prepared IIP before (a) and after (b) the entrapment of Cr(VI).

Figure 3. Effects of (A) the dispersion concentration of F-g-C₃N₄; (B) The amount of IIP solution pre-cast onto F-g-C₃N₄/FTO; (C) The immersion time of IIP@F-g-C₃N₄/FTO into Cr(VI) solution; (D) Solution pH on PEC responses of IIP@F-g-C₃N₄/FTO before (a) and after (b) entrapment of 1.0 µg L⁻¹ Cr(VI), and the variances of the PEC currents (c).

Figure 4. (A) Photocurrent responses of IIP@F-g-C₃N₄/FTO toward Cr(VI) at increasing concentrations (from bottom to top, 0, 0.01, 0.05, 0.1, 0.5, 1.0, 10, 50 and 100 µg L⁻¹) in a

supporting electrolyte of 0.1 M pH 6.0 Tris-HCl. (B) Linear calibration curve. Error bars indicate the standard deviation of five repeated measurements.

Figure 5 Relative photocurrents of IIP@F-g-C₃N₄/FTO in the presence of 10 µg L⁻¹ each compound (a) before and (b) after the addition of 0.1 M EDTA; Relative photocurrents of IIP@F-g-C₃N₄/FTO in a two-component system: 10 µg L⁻¹ Cr(VI) solution with (c) 10 µg L⁻¹ and (d) 200 µg L⁻¹ for each compound (Cr³⁺, Co²⁺, Pb²⁺, Zn²⁺, Ni²⁺, Cd²⁺, Cu²⁺ and Fe³⁺), respectively.

Scheme 1

Table 1. PEC speciation determination of Cr(VI) and Cr(III) in different water samples using the proposed method ($n=3$)

Sample	Added ($\mu\text{g L}^{-1}$)		Found ($\mu\text{g L}^{-1}$)		Recovery (%)		RSD (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Cr (III)	Cr (VI)	Cr (III)	Cr (VI)
Tap water 1	0.00	0.00	0.257	0.108	—	—	3.46	2.45
Tap water 2	0.20	0.20	0.476	0.318	104.2	103.0	1.51	3.10
Tap water 3	0.50	1.00	0.828	0.995	109.4	89.8	3.20	1.80
Yangtze River Water 1	0.00	0.00	0.443	0.320	—	—	3.09	2.86
Yangtze River water 2	0.20	0.20	0.684	0.498	106.5	95.8	1.92	2.42
Yangtze River water 3	0.50	1.00	0.877	1.208	93.0	91.5	1.98	2.00
East Lake water 1	0.00	0.00	0.150	0.055	—	—	2.93	2.15
East Lake water 2	0.20	0.20	0.342	0.268	97.7	105.0	3.25	3.41
East Lake water 3	0.50	1.00	0.686	0.982	105.5	93.0	2.87	2.11

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5