An ultra-sensitive electrochemical sensor of Ni/Fe-LDH toward nitrobenzene with the assistance of surface functionalization engineering

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ABSTRACT

Hypersensitive detection of organic pollutions with high toxicity in drinking water always keeps its challenge in electroanalysis due to their low concentration and electrochemical redox inert. In this work, a novel nano-material modified electrode for the sensitive detection of nitrobenzene (NB) is presented, based on environmental friendly and cost-effective Ni/Fe layered double hydroxides functionalized with sodium dodecyl sulfate (Ni/Fe(SDS)-LDH). Such 2D layered composites were prepared and used to improve the sensitivity for NB detection, due to its good catalytic activity for NB reduction. Besides, the proposed electrode shows a remarkably promoted sensitivity to NB compared to Ni/Fe-LDHs modified one. It is because that the surface modifier SDS can provide more adsorption sites to significantly improve the adsorption of NB, which has been confirmed by the adsorption experiment and the characterization of Fourier transform infrared spectroscopy (FTIR). As a result, an impressive sensing behaviour is achieved at the proposed Ni/Fe(SDS)-LDHs modified electrode with a sensitivity of $15.79 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$. This work provides a promising way to build more advanced nanomaterials to electrochemical detection of organic pollution based on energetically synergizing of adsorption by surface functionalization engineering.

1. Introduction

The environmental pollution in drinking water caused by the discharge of industrial waste is serious. Among the pollutions, nitroaromatic compounds are very harmful to human health [1–3]. They have been classified as highly toxic carcinogens, which remain their carcinogenic activities even at trace level, especially nitrobenzene (NB) [4,5]. NB is a popular product in agricultural chemicals, dyes and explosive industries, and has been considered as one of priority strictly controlled pollutions by many countries [6–9]. After being ingested, NB may cause many disorders in human body, e.g. respiratory failure [10, 11]. Therefore, the sensitive detection of NB is extremely important from eco-toxicological point of view.

At present, various analytical methods have been used to detect NB, such as optical sensor [12,13], gas chromatography [14], high-performance liquid chromatography (HPLC) [15] and so on [16].

However, compared with the above traditional methods, the electrochemical analysis has its impressive advantages, e.g. low cost, easy to operation, rapidity and feasibility for field analysis [17–20]. Otherwise, the development of nanomaterials with excellent properties further brings a new prospect for the electroanalysis of NB. Although a great amount of nanomaterials have been proposed for the sensitive detection of NB, in many cases, the electrochemical performances of nanomaterials are based on the good catalytic activity of noble metal [8,10, 21–24]. It can be explained by the fact that NB is notoriously chemical inert for reduction on electrode [25], since $-\text{NO}_2$ group on benzene ring needs four electrons for the reduction to $-\text{NHOH}$, and six electrons for the reduction to $-\text{NH}_2$ [10]. The multiple electron capture process results in its relatively difficult reduction. Considering the high cost of noble-metal, exploring the cost-effective and noble-metal-free nanomaterials with active catalytic activity for the sensitive electroanalysis of NB remains its emergency demanding task and still a challenge in

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Scheme 1. Fabrication of Ni/Fe(SDS)-LDH and the strategy for NB detection based on synergistic effect of enhanced adsorption and electrocatalysis on Ni/Fe-LDH functionalized with SDS.

electroanalysis field.

In addition to the catalytic activities of nanomaterials, it has been found that their adsorption abilities also play a key role in the improvement of electrochemical performance towards pollution. In this case, the analyte (i.e. NB) can be adsorbed from the homogeneous solution by nanomaterials and accumulated on the electrode surface, where the electrochemical reaction occurs subsequently and giving the electrochemical signal [26]. Considering the importance of both adsorption capacity and catalytic activity, the nanomaterials with good adsorption and catalytic properties are expected to be used as the electrode modifier for the highly sensitive detection of NB.

Layered double hydroxides (LDHs) are really famous for their

intrinsic catalytic activity and amazing adsorption property [27–31]. Various transition metals with mixed valence have been introduced to the formation of the LDH, for instance, Ni/Co-LDH [32,33], Ni/Fe-LDH [34–36], Co/Fe-LDH [37–39], which may bring a great potential to enhance the catalytic activities of LDHs [40]. Actually, it has been reported that multi-metal LDH has a good catalytic performance for the reduction of organic matter, such as metronidazole and 2-nitrophenol [41]. Utilizing this catalytic activity, the LDH is a promising candidate for the electroanalysis of NB. Additionally, LDHs also exhibit good adsorption property to a variety of inorganic pollution, especially anionic species (i.e., As(III) and Cr(VI)) [42,43]. The inorganic anions (CO_3^{2-} , OH^- , F^- , etc.) in the interlayer spacing of LDH materials can exchange with the anionic pollution and thus enhance the adsorption. However, the adsorption abilities of LDHs materials toward organic matter are relatively poor. It is because that the organic matter (i.e. NB) shows a hydrophobic properties, while LDH is opposite hydrophilic. As a result, the adsorption of LDH towards NB is limited, which will further hinder their application in detection NB. To overcome this bottleneck, it is very promising to extend such materials to adsorb organic pollution by the surface functionalization with organic anions. Sodium dodecyl sulfate (SDS) has been extensively applied as the anionic group to modify and functionalize LDH, by which the adsorption ability of LDH can be adjusted by SDS with its hydrophobic affinity [44,45]. Ruan et al. demonstrated that the Ca/Al-SDS-LDHs appeared to have an enhanced adsorption ability toward nitrobenzene in water compared with Ca/Al-Cl-LDH without SDS [45]. You et al. also suggested the Mg/Al-SDS-LDH had a positive effect for the sorption of organic compounds [46]. Therefore, the combination of SDS and Ni/Fe-LDH materials may provide an appealing way to increase the adsorption ability towards NB and thus improve detection performance.

In this work, we fabricated the Ni/Fe(SDS)-LDH, which use SDS as the surface functional anion, to modify the bare glass carbon electrode

Fig. 1. a) SEM, b) TEM and c) HRTEM images of the Ni/Fe-LDH. d) SEM, e) TEM, f) HRTEM images and g) Elemental mapping of as-synthesized Ni/Fe(150 mg SDS)-LDH. Insets in f is the corresponding SAED.

Fig. 2. a) XRD patterns of the Ni/Fe(SDS)-LDH with the various content of SDS from 0 to 150 mg. b) FTIR spectra of Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH.

(GCE) for the electroanalysis of NB. For comparison, the Ni/Fe-LDHs with different content of SDS are prepared, and the effect of the content of SDS on their structure, adsorption ability and electrochemical behaviors are further comprehensively investigated. In detailed, a series of characterizations are performed to give a clear understanding on the structure of Ni/Fe(SDS)-LDH and Ni/Fe-LDH, including scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). With the assistance of surface functionalization engineering by SDS, the Ni/Fe(SDS)-LDH has a remarkably much improved sensing behavior than that of Ni/Fe-LDH, well proving attractiveness of the proposed strategy. Moreover, the stability, the interference and the detection accuracy in practical analysis on Ni/Fe(SDS)-LDH GCE are evaluated with good results.

2. Experiment section

2.1. Chemical reagents

The needed reagents for the preparing of Ni/Fe(SDS)-LDH are $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, CON_2H_4 , NH_4F and SDS. The buffer solution of electrochemical detection are Na_2HPO_4 , NaH_2PO_4 , CH_3COONa , CH_3COOH , KCl , $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$. All these reagents and the NB used in this work were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The reagents were used without

further purification. The deionized (DI) water was purified to meet $>18.2 \text{ M}\Omega \text{ cm}$.

2.2. Synthesis of Ni/Fe(SDS)-LDH and Ni/Fe-LDH

The synthesis of Ni/Fe(SDS)-LDH is operated as following: 1.125 mmol $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.375 mmol $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were added into 30 mL deionized water, and then stirred to forming a clear solution. 0.3 g CON_2H_4 , 0.2222 g NH_4F and different content of SDS (50, 100, 150, 200 mg) were added into above solution and continued to stirring for 4 h. After that, the resulting solution was transferred into a 50 mL Teflon-lined autoclave and kept it at 160°C for 4 h. The final product of Ni/Fe(SDS)-LDH was obtained with thoroughly washing and drying. For the preparation of Ni/Fe-LDH, the process is similar with Ni/Fe(SDS)-LDH, but without the addition of SDS.

2.3. Characterization

The as-synthesized Ni/Fe(SDS)-LDH and Ni/Fe-LDH were characterized by SEM (JEOL JSM-6610LV) equipped with X-ray energy dispersive spectroscopy (EDS), TEM (JEOL JEM-2100), X-ray diffraction (XRD, Panalytical Empyrean diffractometer) with $\text{Cu K}\alpha$ radiation ($1.5418 \text{ \AA}$), FTIR (Nicolet 6700), XPS (VGESCA-LABMKIIX) and Auto Fast Specific Surface Area Analyzer (Brunauer–Emmett–Teller (BET), Tristar II 3020 M). The HPLC was carried out by LC-20AD of Shimadzu.

2.4. Electrochemical measurements

All the electrochemical measurements were performed on electrochemical workstation (CHI-760E, ChenHua Instruments Co., Shanghai, China) with traditional three-electrode system that GCE with 3 mm diameter and Pt wire serve as working electrode and counter electrode, respectively. Besides, all potential values given in this work refer to Ag/AgCl reference electrode. The electrochemical detection method is the differential pulse voltammetry (DPV) with the following parameters: amplitude, 25 mV; increment potential, 4 mV. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) are measured in a solution containing of 5 mM $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.1 M KCl.

The modification of the electrode with LDH is using the traditional drop-coating method. Firstly, 8 mg LDH was dissolved in 2 mL of water to form a homogeneous suspension with sufficient sonication. Then, a 5 μL suspension was dripped on the fresh polished GCE and the electrode was dried naturally at room temperature for further using.

2.5. Adsorption experiments

The adsorption abilities of Ni/Fe(SDS)-LDHs with various SDS (0, 50, 100, 150 mg) content were studied as following: 10 mg Ni/Fe(0–150 mg SDS)-LDHs was well dispersed in 10 mL 0.1 M phosphate buffer solution (PBS, $\text{pH}=7$), which is consistent with electrochemical detection condition. Then the different concentrations of NB (0–400 μM) were added in the above solution forming homogeneous mixture. After the mixture stirring at room temperature for 24 h, the adsorbent was separated from aqueous solution by centrifugation. Herein, the concentrations of NB were quantified with maximum adsorption wavelength of 268 nm by an UV–Vis spectrophotometer (N6000, YuKe Instrument Co., Shanghai, China).

3. Result and discussion

3.1. Strategy for the detection

As shown in Scheme 1, during the preparation of LDH, the added SDS is used as a surfactant to functionalize the surface of Ni/Fe-LDH. A large number of hydroxyl groups on the surface of Ni/Fe-LDH are effectively combined with the sulfonic acid groups of SDS through electrostatic

Fig. 3. a) XPS full spectra and the high-resolution spectra of b) O 1s, c) C 1s and S 2p, d) Fe 2p and Ni 2p of Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH.

attraction. The hydrophobic end of SDS molecular chain is exposed, thereby changing the hydrophilic properties of Ni/Fe-LDH. With the hydrophobic affinity between SDS and NB, the resulting Ni/Fe(SDS)-LDH has an enhanced adsorption ability toward NB. A large amount of NB can be adsorbed on Ni/Fe(SDS)-LDH. Furthermore, with the help of the electrocatalysis of Ni/FeO₆ in Ni/Fe(SDS)-LDH, the adsorbed NB will be effectively reduced to phenylhydroxylamine and nitrosobenzene with four-electron and two-electron transfer, respectively [21]. It is known that the reduction of NB to phenylhydroxylamine is an irreversible process, while the phenylhydroxylamine and nitrosobenzene are the well-defined redox couple [47]. Three peaks are all identified in CV, but only one peak appears using DPV, which was used as the detection signal of NB. An excellent electrochemical performance is achieved based on the synergistic effect of adsorption and electrocatalysis on Ni/Fe(SDS)-LDH. More details will be discussed later.

3.2. Characterization of Ni/Fe(SDS)-LDH

Fig. 1 illustrates the SEM and TEM images of pristine Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH. The Ni/Fe-LDH without SDS shows typical hollow sphere with a particle size of about 6 μm , composed of many hierarchically structured sheets in detail (Fig. 1a and b). This uniform hollow hierarchical structure is good for the enhancement of specific surface area. The lattice spacing of 0.231 nm presented in Fig. 1c is perfectly corresponding to the (015) plane in Ni_{0.75}Fe_{0.25}(CO₃)_{0.125}(OH)₂. Apparently, Ni/Fe(SDS)-LDH exhibits a rather different appearance after the addition of 150 mg SDS in Ni/Fe-LDH (Fig. 1d and e). The structure of Ni/Fe(150 mg SDS)-LDH shows typical thin nanosheets rather than sphere. For details, the effect of SDS amounts on the morphology of Ni/Fe-LDH is also studied. As shown in Fig. S1 (in Supplementary Materials), with the increasing of SDS concentration (0–150

mg), the morphology of Ni/Fe-LDH gradually change from spherical-like structure to dispersed transparent and flocculent nanosheets, which well prove that the introduction of SDS could functionalize the surface of Ni/Fe-LDH hollow sphere.

Furthermore, the XRD patterns of Ni/Fe(SDS)-LDH with SDS content from 0 to 150 mg are recorded. Although the significant differences can be observed between the morphologies of Ni/Fe(50, 100, 150 mg SDS)-LDH and Ni/Fe-LDH, their XRD patterns (Fig. 2a) can all well index to the XRD pattern of Ni_{0.75}Fe_{0.25}(CO₃)_{0.125}(OH)₂·0.38H₂O (JCPDS No. 40-0215) [48]. It suggests the addition of 0–150 mg SDS is unable to change the structure of Ni/Fe(SDS)-LDH, but only slightly affect the crystallization which resulted in the decrease of diffraction peaks intensity. The lattice spacing at 0.260 nm and the selected area electron diffraction (SAED) in Fig. 1f all confirm the crystal face of Ni/Fe(150 mg SDS)-LDH. As illustrated in Fig. 1g and Fig. S1e, the uniform distributions of Ni, Fe, O and F are observed on Ni/Fe(150 mg SDS)-LDH and Ni/Fe-LDH, while additional existence of S is found in the elemental maps of Ni/Fe(150 mg SDS)-LDH nanosheets, which belongs to SDS. The different content of S are determined to identify the real loading amount of SDS into Ni/Fe(SDS)-LDH by EDS (Fig. S2). It is clearly that the atomic ratio of S/(Fe + Ni) (9.87, 20.75, 27.93% for 50, 100, 150 mg SDS, respectively) are generally grows as the increase of SDS, well proving that the added SDS during the preparation process are effectively coated on the surface of Ni/Fe(SDS)-LDH. The appearance of some new vibration peaks in FTIR spectra of Ni/Fe(150 mg SDS)-LDH compared with Ni/Fe-LDH further reveals the presence of SDS (Fig. 2b), such as the peaks at 2860 and 2937 cm⁻¹ referring to the -CH₂ groups [49], the bands at 1046 and 1165 cm⁻¹ ascribing to the S=O bonds of SDS [50]. The other peaks should be attributed to the characteristic vibration of LDH, which have been marked in Fig. 2b.

It is worth mentioned that more content of SDS (200 mg) added into

Fig. 4. a) CV curves of Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH modified GCEs in 0.1 M PBS (pH = 7.0) without and with 100 μM NB, respectively. b) DPV response of bare GCE, Ni/Fe-LDH and Ni/Fe(0–200 mg SDS)-LDH toward 100 μM NB at a scan rate of 0.04 V s⁻¹ in 0.1 M PBS (pH = 7.0), respectively.

Ni/Fe-LDH has also been investigated. As shown in Fig. S3a, the SEM of Ni/Fe(200 mg SDS)-LDH also has a typical nanosheet structure. However, the diffraction peaks of Ni/Fe(200 mg SDS)-LDH change remarkably compared with Ni/Fe(0–150 mg SDS)-LDH, indicating the reconstruction of Ni/Fe-LDH in presence of excess SDS [51]. Large amount works have proved that SDS can exchange with the inorganic anions in the interlayer of LDH (including CO₃²⁻, OH⁻, F⁻, etc.) and intercalate the interlayer, which can cause clear negative shift of (003) peak at 11.41° to lower 2θ like the phenomenon in Fig. S3b [52,53]. The sharp increase of S/(Fe + Ni) ratio (47.92%) (Fig. S3c) and obvious color change (Fig. S4f) of Ni/Fe(200 mg SDS)-LDH further give the evidence that the excess SDS (200 mg) may partly intercalate into the interlayer of Ni/Fe-LDH. In fact, LDH intercalated with SDS is possible conducive to enhance the adsorption of NB. However, the hydrophobic property of Ni/Fe(200 mg SDS)-LDH also increase dramatically, resulting in its poor dispersibility in water and even difficult to modify on GCE surface by drop-coating method in our work. The water contact angle test between Ni/Fe(0–200 mg SDS)-LDH also proves our point (Figs. S4a–e). As the increase of SDS, the contact angles increase (15.6, 20.1, 44.3, 72.9° for 0, 50, 100, 150 mg SDS, respectively) and reach maximum at 200 mg SDS (130.8°). This result is consistent with that found in another works about the SDS intercalated LDH [54,55]. The strong hydrophobic properties of Ni/Fe(200 mg SDS)-LDH not only have an adverse effect on the control of electrode morphology, but also very unfavorable for the electrolyte to be close to electrode surface, which will both lead to

decreased electrochemical signal although with excellent adsorption ability [56,57]. The poor detection performance of Ni/Fe(200 mg SDS)-LDH will be discussed below. Therefore, we chose 150 mg as optimal amount of SDS and following discussion is mainly focused on Ni/Fe(150 mg SDS)-LDH.

We compare the XPS spectra of Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH (Fig. 3) to further understand the changes of binding energy in LDH structure before and after functionalizing with SDS. Besides the emergence of S 2s and S 2p (Fig. 3a), the obvious decrease of the -OH/O_{total} ratio (Fig. 3b) in Ni/Fe(150 mg SDS)-LDH compared with Ni/Fe-LDH means that the -OH on Ni/Fe-LDH is combined with -SO₃ of SDS. Indeed, the positive shift of O 1s (Fig. 3b) in Ni/Fe(150 mg SDS)-LDH contrast to that in Ni/Fe-LDH further proves this point. Meanwhile, there is almost no change about the Fe 2p and Ni 2p, suggesting the functionalization of SDS does not affect the structure of octahedral MO₆ (M = Ni and Fe) in LDH. Furthermore, the BET surface areas of Ni/Fe(150 mg SDS)-LDH and Ni/Fe-LDH are investigated in Fig. S5. With the addition of SDS, the surface area of Ni/Fe(150 mg SDS)-LDH decreases a lot (9.83 m²/g) compared with Ni/Fe-LDH (40.25 m²/g). This is possibly due to the large change in morphology. The original hollow spherical Ni/Fe-LDH with a large surface area has become nanosheet with smaller surface area. It is worth noting that in previous works, a consensus was reached on the pursuit for large specific surface area to improve the adsorption capacity of nanomaterial. However, herein, Ni/Fe(SDS)-LDH with smaller surface area has better adsorption capacity to NB, resulting from more effective hydrophobic adsorption sites (i.e. SDS) on Ni/Fe(SDS)-LDH.

3.3. Electrochemical characterization

The electrochemical characterization of CV and electrochemical impedance resistance (EIS) on Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH are respectively examined (Fig. S6). After modified with Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH, a sharp decrease of CV current and increase of EIS value are shown. It is the evidence that the conductivities of both LDH are small, especially for Ni/Fe(150 mg SDS)-LDH. It is foreseeable to know that SDS is non-electronic conductor. However, this decreased conductivity has an ignorable impact on NB detection. Prior to detection, the electroanalytical conditions are optimized in Fig. S7. As shown in Fig. S7a, NB has the highest DPV current in phosphate buffer solution (PBS), due to PBS helps its adsorption of NB on Ni/Fe(150 mg SDS)-LDH (proved in below). When the pH value of PBS gradually increases to 7.0, the reduction current of NB increases accordingly, and the further increases of pH lead to the decrease of electrochemical signal. It is suggested that the most favorable condition is under neutral pH (7.0). Furthermore, the effect of pH value on the reduction peak potential (E_{pc}) of NB is studied in Fig. S8. The peak position changes linearly with pH, $E_{pc} = -0.40 - 0.029$ pH, suggesting that protons are involved in the reduction process of NB. This is very consistent with Nernst equation, $E_{pc} = E^0 - (0.059 \text{ m/n}) \text{ pH}$, where the m and n represent the number of protons (m) and electrons (n) [57]. As shown, the m/n in NB reduction is about 1/2, indicating more electrons participate into such a reduction process than protons and electron plays a more important role. The effect of accumulation time on DPV response to 100 μM NB is shown in Fig. S7c. The increase in accumulation time is good for adsorbing more NB, but it will reach a saturation value at about 150 s. At last, we chose the optimized condition as following: in 0.1 M PBS with a pH value of 7, and the accumulation time is 150 s.

3.4. Electrochemical detection of NB

The electrochemical performance of NB on Ni/Fe(150 mg SDS)-LDH GCE are firstly evaluated by CV. For contrast, the CV response of Ni/Fe-LDH GCE to 100 μM NB is also examined (Fig. 4a). There is no redox response on both electrodes in the absence of NB. As injected with 100 μM NB, three prominent redox peaks are captured, including a pair of

Fig. 5. DPV of a) Ni/Fe-LDH and b) Ni/Fe(150 mg SDS)-LDH with individual addition of different concentration NB from 1 to 350 μM into 0.1 M PBS (pH = 7.0), respectively. c) and d) are the calibration plots of the reduction currents of NB against its concentrations on Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH. Insets in c and d are partial magnification in low concentration (1–10 μM) of NB. The confidence intervals are calculated with a level of 95%.

Table 1

A comparison of electrochemical performance (including linear range, sensitivity and LOD) of electrodes for DPV detection of NB.

Electrode	Linear range (μM)	Sensitivity ($\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$)	LOD (μM)	Ref.
Pd-polymer-silica GCE	1–1900	0.371	0.06	[22]
$\gamma\text{-Al}_2\text{O}_3$ GCE	0.5–145.5	1.27	0.15	[47]
Au NPs-mesoporous silica GCE	0.1–2500	0.341	0.015	[21]
Au NPs GCE	0.1–600	1.01	0.016	[10]
Co-MOF-MPC	0.5–15	1780	0.21	[59]
Ag NPs-POSS/RGO GCE	4–1260	–	0.08	[60]
PAA-Ag NPs GCE	10–600	–	1.68	[61]
Ni/Fe-LDH	1–10;	6.21;	0.327	This work
	10–100;	3.85;		
	100–350	1.98		
Ni/Fe(SDS)-LDH	1–10;	15.79;	0.093	This work
	10–100;	8.55;		
	100–350	6.32		

NPs: nanoparticles; GCE: glass carbon electrode; Co-MOF-MPC: cobalt-based MOF and macroporous carbon (MPC) composite; RGO: reduced graphene oxide; POSS: polyhedral oligomeric silsesquioxane; PAA: poly(amic) acid.

well-defined redox peaks (O1 and R1) and an irreversible reduction peak (R2) on Ni/Fe(150 mg SDS)-LDH GCE. The observed R2 at about -0.70 V is ascribed to the peak of NB reduction to phenylhydroxylamine with four electron transfer process. Meanwhile, the redox couple of O1 and R1 at -0.034 and -0.12 V are respectively corresponding to the redox between phenylhydroxylamine and nitrosobenzene with two electron transfer [21,57]. Otherwise, the redox current of NB on Ni/Fe(150 mg SDS)-LDH is higher than that on Ni/Fe-LDH GCE, giving the evidence of effective NB detection on Ni/Fe(150 mg SDS)-LDH.

The DPV response of Ni/Fe(SDS)-LDHs with various content of SDS

Fig. 6. FTIR spectra of Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH with uptake of NB.

have been explored in Fig. 4b. The response current of Ni/Fe(0–150 mg SDS)-LDHs raise steadily with the increase of SDS content. It is because that the modification of SDS is very benefit for the adsorption of NB, which can lead to the improvement of electrochemical signal. However, the current of Ni/Fe(SDS)-LDH with 200 mg SDS becomes lower than that of 150 mg. As discussed above, Ni/Fe(200 mg SDS)-LDH cannot be modified uniformly on the surface of GCE due to its high hydrophobicity, and thus leading to a reduced response. For contrast, Ni/Fe(150 mg SDS)-LDH with both good adsorption properties and water-dispersibility shows the best electroanalytical performance to NB.

Fig. 7. NB removal efficiency adsorbed on a) Ni/Fe-LDH with 0–150 mg SDS at the concentration of 50, 100, 200, 300 and 400 μM NB, respectively; b) Ni/Fe(150 mg SDS)-LDH with different buffer solution to 100 μM NB; c) Ni/Fe(150 mg SDS)-LDH with different pH of 0.1 M PBS to 100 μM NB.

We further investigated the DPV electrochemical response of Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH toward NB at different concentrations (Fig. 5), low level (1–10 μM), middle concentration (10–100 μM) and high level (100–350 μM), respectively. Both Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH modified GCE have well-defined response as the concentration of NB increase (Fig. 5a and b). The Ni/Fe(150 mg SDS)-LDH GCE has three diverse liner relationships in the concentration range of 1–350 μM, expressing as follows:

$$j_1 (\mu\text{A cm}^{-2}) = (15.79 \pm 0.41) C (\mu\text{M}) + (126.97 \pm 2.57) \quad (1-10 \mu\text{M}).$$

$$j_2 (\mu\text{A cm}^{-2}) = (8.55 \pm 0.25) C (\mu\text{M}) + (200.66 \pm 3.17) \quad (10-100 \mu\text{M}).$$

$$j_3 (\mu\text{A cm}^{-2}) = (6.32 \pm 0.11) C (\mu\text{M}) + (366.45 \pm 4.25) \quad (100-350 \mu\text{M}).$$

The j is the current density of DPV peak of NB, which is calculated by Current/Area. Area is real electrochemical surface areas (ECSA) of Ni/Fe(150 mg SDS)-LDH GCE, according to the Randles–Sevcik equation, $i_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} \nu^{1/2}$ in Fig. S9. It is clearly shown that the sensitivities decreases with increased concentration in different concentration range, due to the decreased effect in adsorption enhancement on Ni/Fe(150 mg SDS)-LDH and reaching adsorption saturation at higher concentration. This phenomenon of segmented detection sensitivity is also very common in literatures [56,57]. With 3σ method (signal

to noise ratio of 3 ($S/N = 3$)) defined by IUPAC [58], the limit of detection (LOD) is 0.093 μM, which is below than the maximum permissible limit of NB in drinking water guided by United States environmental protection agency (0.138 μM). The sensitivity of Ni/Fe-LDH toward NB is also investigated as (6.21 ± 0.35) , (3.85 ± 0.17) , $(1.98 \pm 0.06) \mu\text{A } \mu\text{M cm}^{-2}$ in different concentration range. The LOD of Ni/Fe-LDH is further calculated to be 0.327 μM. Although the sensitivity of Ni/Fe-LDH is relatively low over all concentration range compared to Ni/Fe(150 mg SDS)-LDH, it is very advantageous in contrast to those electrodes reported in other articles (Table 1), indicating the catalysis and adsorption of Ni/Fe-LDH towards NB. It can conclude that compared with Ni/Fe-LDH GCE, the electrochemical performance of Ni/Fe(150 mg SDS)-LDH GCE has been greatly improved. Otherwise, compared with the previously reported sensors based on other nanomaterials (Table 1), the analytical performance of Ni/Fe(150 mg SDS)-LDH GCE is considerable, which can used for sensitive analysis of NB. This can attribute to the addition of SDS and its enhancement of adsorption to NB, suggesting that the combination of adsorption and catalysis is very valuable for the detection of organic pollutions.

Fig. 8. Interference studies of a) p-nitrophenol (PNP), b) o-nitrophenol (ONP), c) 1,4-dihydroxybenzene (1,4-DHB), d) phenol and e) 2,4-dinitrotoluene (2,4-DNT) toward 100 μM NB on Ni/Fe(150 mg SDS)-LDH GCE. f) Current change of 100 μM NB at presence of 100 μM PNP, ONP, 1,4-DHB, phenol, 2,4-DNT, Hg^{2+} , Cd^{2+} , SO_4^{2-} and F^- , respectively.

3.5. Adsorption behavior of Ni/Fe(SDS)-LDH

In order to study the difference in NB adsorption on Ni/Fe-LDH and Ni/Fe(150 mg SDS)-LDH, we investigated their FTIR spectra after uptake with NB (Fig. 6). The vibration peak at 1521 cm^{-1} , attributed to benzene, clearly proves that NB is adsorbed on both LDHs. However, the stronger peak intensity of benzene on Ni/Fe(150 mg SDS)-LDH well demonstrates that its adsorption capacity is higher than that of Ni/Fe-LDH, which can lead to a higher response of NB.

The various adsorption behaviors of Ni/Fe(SDS)-LDH (including with 0, 50, 100, 150 mg SDS) toward NB with different concentration (including 50, 100, 200, 300 and 400 μM NB) have been detailly explored (Fig. 7a). As presented, the order of removal efficiency of Ni/Fe(SDS)-LDH is always $150\text{ mg} > 100\text{ mg} > 50\text{ mg} > 0\text{ mg}$ SDS no matter the concentration of NB. This result perfectly confirms the truth of the enhancement effect of SDS on the adsorption to NB. It is also consistent with the order of DPV response current of Ni/Fe(0–150 mg SDS)-LDH in Fig. 4b, well proving the combination of adsorption and catalysis is effective. Furthermore, the removal efficiency of all Ni/Fe(SDS)-LDHs

gradually decrease as the concentration of NB increases (100–400 μM , Fig. 7a). This is due to that the adsorption of NB is reach maximum equilibrium at higher concentration of NB. It is also the possible reason for the different sensitivities of Ni/Fe(150 mg SDS)-LDH at various concentration range (Fig. 5d). In addition, the adsorption behaviors of Ni/Fe(150 mg SDS)-LDH to NB in diverse buffer solution and pH value of PBS are examined in tandem (Fig. 7b and c). As expected, the Ni/Fe(150 mg SDS)-LDH has the biggest removal efficiency at PBS with a pH of 7, completely consistent with the results obtained from electrochemical optimization condition in Fig. S7. Now, it is clear that adsorption plays key role in electrochemical analysis of NB on Ni/Fe(150 mg SDS)-LDH.

3.6. Reproducibility, stability, interference and the practical application

As for achieving the analysis of actual water samples, the reproducibility, stability, anti-interference of the fabricated electrode are evaluated for detection of NB at Ni/Fe(150 mg SDS)-LDH GCE. After consecutive 20 cycles of DPV scanning, the current of 350 μM NB at Ni/Fe(150 mg SDS)-LDH GCE decreased slowly (Fig. S10a). It is because

Fig. 9. The detection of NB in real sample collected from mining subsidence area on Ni/Fe(150 mg SDS)-LDH GCE. Inset is corresponding linear calibration plot. The confidence intervals are calculated with a level of 95%.

Table 2

Electrochemical detection of spiked NB in real water (underground water and tap water of Huaibei City) at the Ni/Fe(150 mg SDS)-LDH GCE (n=3). HPLC method is chose as a reference method to compared with electroanalysis.

	concentrations of NB		RSD (%)	Recovery (%)	HPLC (μM)
	Added (μM)	Found (μM)			
Underground water 1	7	7.31 ± 0.22	3.56	95.75	7.04
Underground water 2	15	14.82 ± 0.38	7.61	98.80	15.12
Tap water 1	7	6.41 ± 0.39	4.32	91.57	7.07
Tap water 2	15	15.22 ± 0.35	5.95	101.47	15.35
Tap water 3	20	21.54 ± 0.93	8.29	107.70	20.68

that the adsorbed and reduced nitrobenzene cannot be released from the Ni/Fe(150 mg SDS)-LDH in time and then inhibit the continuous accumulation of NB from solution to electrode modifier. The slight decrease could be avoided by removing the residual NB by using a fresh base solution. We compared the DPV current of 350 μM NB under optimal conditions at three Ni/Fe(150 mg SDS)-LDH modified GCEs (Fig. S10b), which were prepared with same process. It is found that the peak shape and peak current of NB can be reproduced well, and a good relative standard deviation (RSD) are obtained to be 5.7%. The lifetime of the sensor is further investigated. As shown in Fig. S10c, the electrochemical response toward 100 μM NB on the modified electrodes, which has been respectively stored in the air for 1–3 weeks, are similar with the freshly fabricated electrode. There is no significantly change after long-time storage, well indicating the lifetime and reproducibility of the sensor is excellent. The results all indicate the excellent reproducibility and stability of Ni/Fe(150 mg SDS)-LDH.

In many cases, there will be various kinds of organic pollutants in the water environment, and they will interfere with each other. For the interference study of NB, p-nitrophenol (PNP), o-nitrophenol (ONP), 1,4-dihydroxybenzene (1,4-DHB), phenol, and 2,4-dinitrotoluene (2,4-DNT) are selected as the interferences, which have very similar properties (including adsorption properties and electrochemical behaviour) with NB. When the concentration of PNP is relatively low (0–80 μM), there is almost no interference to the detection of 100 μM NB, including

current and peak shape (Fig. 8a). As the concentration increases (80–120 μM), although the current does not change, a new peak appears at the negative position of NB. The emergent peak is the response of PNP. The obvious changes of the peak shape and current of NB are also obtained after the addition of 2,4-DNT and phenol, especially for 2,4-DNT. It is because the reduction of –NO₂ on 2,4-DNT has close peak position with NB due to their similar electrochemical behavior. These results show that when there are other organic compounds, it will interfere with the detection of NB, typically for these have electrochemical activity. More works are need to solve the poor selectivity of the electrochemical sensor. However, the presence of ONP and 1,4-DHB have negligible interferences on the NB, although they have similar adsorption properties as organic matter. It is further satisfactory that the inorganic cations and anions in water have almost no negative effect on the detection of NB even with higher concentration (0–1000 μM, Fig. S11).

The natural lake water samples were collected from the Nanhu Lake in Huaibei City, Anhui Province, China, and used to illustrate the accuracy of the proposed electrode in practical analysis. Nanhu Lake is a natural lake with a water area of 3.3 square kilometers formed in a coal mining subsidence area, which contains a lot of inorganic ions and biological organic matters. With simply filtering out the insoluble substances in the actual water sample, the buffer solution is obtained by mixing the 0.1 M PBS (pH 7.0) solution with real water in a volume ratio of 9:1. As found in Fig. 9 that in actual water environment, Ni/Fe(150 mg SDS)-LDH GCE can also achieves a sensitive detection of NB. Interfering ions present in natural water will not adversely affect our detection system, and the resulting sensitivity is only slightly reduced compared to pure water environment. Otherwise, different kinds of natural aqueous systems including underground water and tap water in Huaibei City were further determined. As given in Table 2, the Ni/Fe(150 mg SDS)-LDH GCE has a good performance to NB owning satisfied recovery and RSD in the above water environment. Furthermore, the NB spiked in real samples (including underground water and tap water) are also detected by a reference method of HPLC method to compare with electroanalytical results. As shown in Fig. S12 and Table 2, the found content of NB detected by electroanalysis is near the result of HPLC, as well as the added concentration. This result indicates the NB detection accuracy of electroanalysis on Ni/Fe(150 mg SDS)-LDH GCE is considerable and reliable. In a word, the fabricated Ni/Fe(150 mg SDS)-LDH GCE has a great potential for the practical application of actual water samples with a high accuracy and good reliability.

4. Conclusion

In summary, a novel chemically modified electrode for sensitive detection of the organic pollution NB has been described, based on the combination of the adsorption and catalytical properties of the Ni/Fe(SDS)-LDH composite. Compared to the Ni/Fe-LDHs modified electrode, the proposed sensor has shown a significantly improved detection performance for NB due to the improved adsorption capability with the assistance of surface functionalization engineering of SDS. After being adsorbed, the NB on Ni/Fe(SDS)-LDH can be reduced by the catalyst of Ni/FeO₆, offering standout performance for NB detection. A considerable sensitivity and LOD are achieved on Ni/Fe(SDS)-LDH even exposure with smaller specific area. The excellent electrochemical behavior indicates that the significant synergistic effect of enhanced adsorption and catalysis of Ni/Fe(SDS)-LDH is really effective for the sensitive detection of NB. Moreover, the practical application of the proposed sensor has been carried out for the electroanalysis of NB in the real water samples collected from mining subsidence area.

Credit author statement

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Methodology, Formal analysis. Min Zhu, Visualization. Feng Zhang, Investigation, Visualization. Bo-Ya Zhang, Methodology, Investigation. Tian-Jia Jiang, Writing – review & editing. Yong-Xing Zhang, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

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

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Appendix A. Supplementary data

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