

# Application of Ni-Al Layered Double Hydroxides/Graphene Composites for Highly Efficient Electrochemical Detection of Methyl Parathion

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This work developed a one-step coprecipitation method to synthesize Ni-Al layered double hydroxides decorated graphene nanosheets composite (Ni-Al LDHs/Gr). The obtained Ni-Al LDHs/Gr nanosheets can efficiently capture organophosphate pesticide of methyl parathion (MP) and achieve its highly sensitive analysis. This is probably arising from the excellent conductivity of graphene and the high enrichment effect of Ni-Al LDHs through selective intercalation. The developed MP sensor shows a high detection sensitivity, good selectivity and reliable stability. This work shows prospect for developing other electrochemical sensors for analysis of organophosphate pesticide.

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**Keywords:** Layered double hydroxides; Graphene; Electrochemical; Methyl parathion;

## 1. INTRODUCTION

Organophosphate pesticides (OPs), as high hazardous insecticides, have been extensively used to manage pest problems mainly in agriculture field. The mechanism of toxicity of OPs is attributed to their disfunction of neurotransmitter enzyme, acetylcholinesterase (AChE), and thus leading to accumulation of acetylcholine in body [1-2], which finally results in respiratory paralysis and even death for both animals and humans. Therefore, in view of health protection and public security, it is urgently needed to develop a simple, sensitive and reliable method for determination of ultra-trace OPs residue in complex matrices such as crops. Among various detection strategies, electrochemical methods stand out due to its characteristics of simplicity, high detection sensitivity and good selectivity.

Developing materials with both high electrocatalytic activities and excellent adsorption ability toward OPs is vital for fabricating a high-performance electrochemical OPs sensor. So far, various

materials such as highly conductive metal nanoparticles [3,4], carbon nanotubes [5-7], graphene [4,8] and good adsorptive  $\text{ZrO}_2$  [9],  $\text{Al}_2\text{O}_3$  [10], layered double hydroxides (LDHs) [8,11] as solid-phase extraction have been reported for sensitive determination of OPs. Recently, LDHs, as unique two-dimensional layered structure, have attracted much research interest in electrochemical sensors. Ni-Al LDHs, with divalent  $\text{Ni}^{2+}$  ion and trivalent  $\text{Al}^{3+}$  ion, are ideal solid-phase extraction for OPs through selectively intercalated into the interlayer space of LDHs [10-12]. Despite the desirable properties, the performance of these materials needs further improvement due to their low conductivity and the resultant low electron transfer rate. Integration of Ni-Al LDHs with conductive support is an effective strategy to improve the performance of LDHs based electrochemical sensors.

In this work, graphene (Gr) was employed as conductive support and intercalation materials to be introduced in the Ni-Al LDHs composites. One-step coprecipitation method was first used to synthesize Ni-Al LDHs/Gr composites, which can improve the electron transfer and significantly promote the enrichment of OPs. Therefore, the Ni-Al LDHs/Gr composites could realize the rapid, selective and sensitive stripping voltammetric determination of the typical OPs species, methyl parathion (MP).

## 2. EXPERIMENTAL SECTION

### 2.1. Reagents and apparatus

All reagents including  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , cetyltrimethylammonium bromide (CTAB), HAc, NaAc, MP, Dantox and other various salts were purchased from Sinopharm Chemical Reagent Co., Ltd and used as received without further purification. Graphene oxide (GO) was obtained from Nanjing XFNANO Materials Tech Co., Ltd. Acetate-buffered solutions (ABS, 0.1 M, pH 5.0) were prepared with 0.1 M HAc and NaAc. The obtained ABS was utilized as electrolyte solutions throughout the whole experiments. 18.2 M $\Omega$  cm deionized water was used for preparing various solutions.

Field emission scanning electron microscope (FESEM, Hitachi SU-8010) was employed to characterize the morphologies of the synthesized Ni-Al LDHs and Ni-Al LDHs/graphene composites. Electrochemical experiments comprising of cyclic voltammetry (CV), and square-wave voltammetric (SWV) analysis were performed on a CHI 660D electrochemical station (Shanghai Chenhua Instrument Co. Ltd., China). The conventional three-electrode system was used with Ni-Al LDHs/Gr composites modified electrode as the working electrode, a platinum wire as auxiliary electrode, and a saturated calomel electrode (SCE) as reference electrode.

### 2.2. Synthesis of Ni-Al LDHs/Gr composites

One-step coprecipitation method was used to synthesize Ni-Al LDHs/Gr composites according to the following procedure: First, 0.058 g of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.038 g of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 0.40 g of CTAB were dissolved into 25 mL solvent constituted by 2:1 volume ratio of methanol and deioned

water under the help of ultrasonication for 10 min. Then, addition of 0.0125 g of GO into the above mixture was performed under further ultrasonication for 2 h until complete dissolution. After that, the resultant solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and heated to 180 °C for retaining 24 h. After cooled to room temperature, the Ni-Al LDHs/Gr products were obtained by centrifugation and repeatedly washed with deionized water and ethanol, and finally dried at 100 °C for 24 h. Ni-Al LDHs was also synthesized using the same method except for the addition of GO.

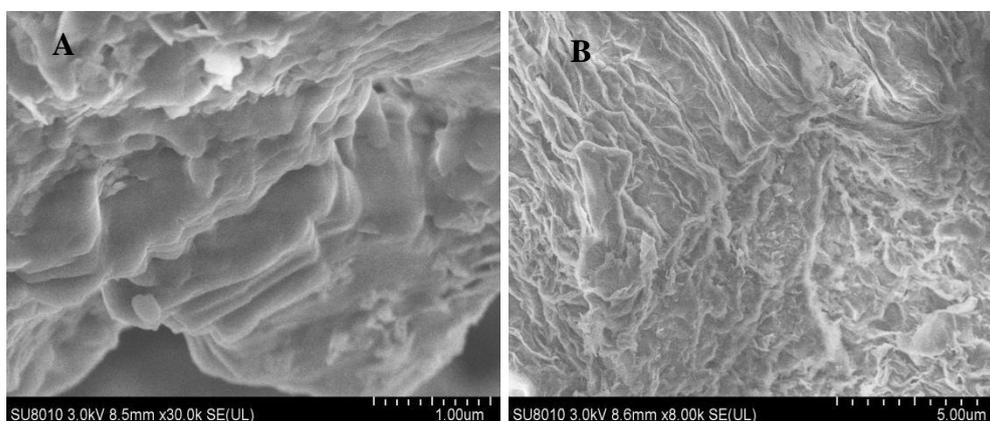
### 2.3. Electrochemical detection of MP by Ni-Al LDHs/Gr composites modified electrodes

Prior to modification, the bare glassy carbon electrode (GCE) was polished using 0.3 and 0.05  $\mu\text{m}$  alumina powder sequentially, sonicated with deionized water and ethanol. 10  $\mu\text{L}$  1  $\text{mg mL}^{-1}$  of Ni-Al LDHs/Gr composites aqueous dispersion was dropped onto the surface of GCE. After dried at room temperature, Ni-Al LDHs/Gr composites modified GCE (Ni-Al LDHs/Gr/GCE) was prepared. For comparison study, the Ni-Al LDHs modified GCE (Ni-Al LDHs/GCE) and GO modified GCE (GO/GCE) were also prepared according to the above process similar to that of Ni-Al LDHs/Gr/GCE.

For electrochemical detection of MP, the Ni-Al LDHs/Gr/GCE was first dipped into a stirred sample solution containing a certain concentration of MP for 10 min, and rinsed with water. After that, it was transferred into the blank buffer solution (0.1 M, pH 5.0 ABS) for SWV quantitative measurements. The regeneration of electrode was achieved by continuous SWV scanning until the anodic current response disappeared.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of Ni-Al LDHs/Gr composites



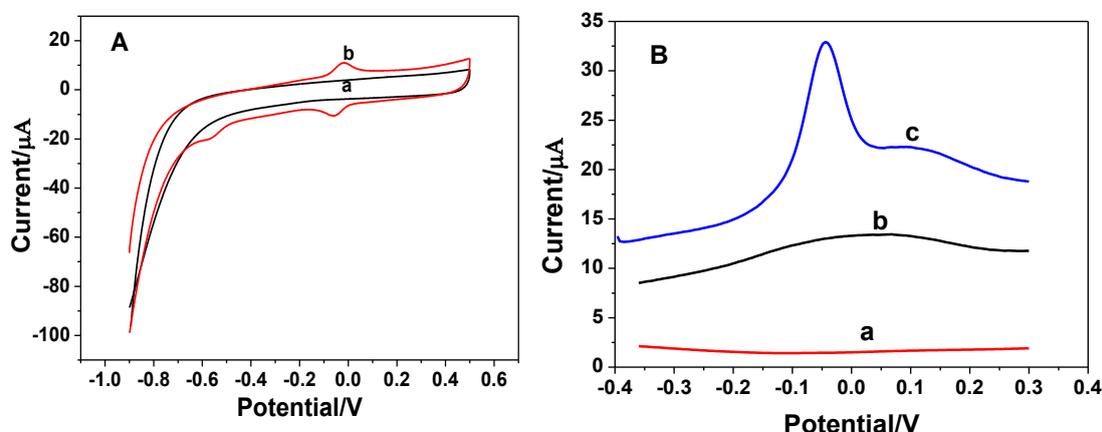
**Figure 1.** SEM images of Ni-Al LDHs (A) and Ni-Al LDHs/Gr composites (B).

The typical morphology of the Ni-Al LDHs and Ni-Al LDHs/Gr composites is characterized by SEM, the results of which is shown in Fig. 1A and 1B. As can be seen, the Ni-Al LDHs consists of many stacked and layered nanosheets with the thickness of 20-40 nm. After introduction of Gr, a thin

layer of wrinkled and flake-like shape with plenty of corrugations and scrollings can be observed, indicating successful preparation of Ni-Al LDHs/Gr composites.

### 3.2. Electrochemical responses of Ni-Al LDHs/Gr/GCE to MP

Fig. 2A exhibits the CVs of Ni-Al LDHs/Gr/GCE in 0.1 M ABS (pH 5.0) before (a) and after (b) preconcentration of 2  $\mu\text{g/mL}$  MP for 10 min. As observed, no obvious redox peak appeared in ABS without enrichment of MP (curve a) in the present potential range. However, after capture of MP on Ni-Al LDHs/Gr/GCE, a pair of reversible redox peaks located at potentials of -0.017 V and -0.054 V and an irreversible cathodic peak at -0.564 V were observed (curve b). The reversible redox peaks can be assigned to a two-electron-transfer process between hydroxylamine (-NHOH) and nitroso groups (-NO). The irreversible cathodic peak corresponds to the reduction of the nitro group to the hydroxylamine group. The obtained results are consistent with others reported elsewhere for nitroaromatic OPs [12-16].

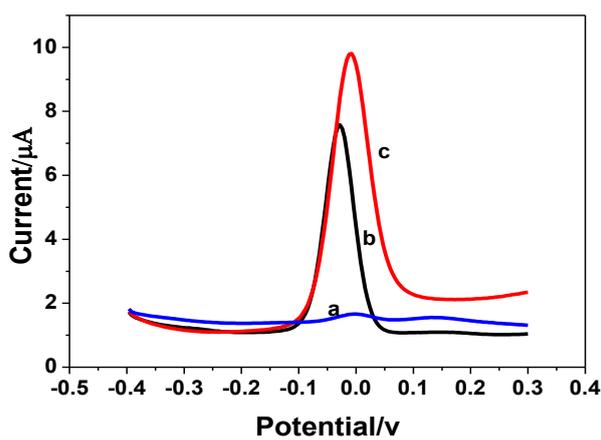


**Figure 2.** A: CVs of Ni-Al LDHs/Gr/GCE in 0.1 M ABS (pH 5.0) before (a) and after (b) preconcentration of 2  $\mu\text{g/mL}$  MP for 10 min; B: SWVs obtained at Ni-Al LDHs/Gr/GCE in blank ABS (a), the ABS solution containing 2  $\mu\text{g/mL}$  MP without preconcentration (b), and ABS solution after preconcentration in 2  $\mu\text{g/mL}$  MP for 10 min (c). SWV conditions: frequency, 25 Hz; potential increment, 4 mV; amplitude of the square-wave, 20 mV.

Square wave voltammetry (SWV) is a more sensitive technique than CV, thus SWV technique was used to investigate the electrochemical response of the Ni-Al LDHs/Gr/GCE to MP. Before SWV determination, the Ni-Al LDHs/Gr/GCE was first immersed into MP solution (pH 5.0) for 10 minutes to preconcentration of MP, and then carefully washed with deionized water. Through this step, the MP captured Ni-Al LDHs/Gr/GCE was obtained. As shown in Fig. 2B, there was no oxidation peak observed at Ni-Al LDHs/Gr/GCE in blank ABS (curve a). However, an obvious SWV anodic peak with sharp shape appeared at -0.044 V for MP captured Ni-Al LDHs/Gr/GCE in blank ABS (curve c). When direct measurement in MP sample solution at Ni-Al LDHs/Gr/GCE (curve b), there was only a low and broad anodic peak, which was significantly lower than MP captured Ni-Al LDHs/Gr/GCE.

This may be due to the specific host-guest interaction between Ni-Al LDHs/Gr and MP. Obviously, the solid phase extraction through the intercalation of MP into the Ni-Al LDHs/Gr composite, results in the enrichment of MP, and thus the prominent current enhancement at Ni-Al LDHs/Gr/GCE.

To exhibit the priority of Ni-Al LDHs/Gr composites towards MP detection, the SWVs of Ni-Al LDHs/GCE (a), Gr/GCE (b) and Ni-Al LDHs/Gr/GCE (c) in 0.1 M ABS (pH 5.0) after preconcentration of 2  $\mu\text{g/mL}$  MP were compared and displayed in Fig. 3. Obviously, the Ni-Al LDHs/Gr/GCE shows the largest anodic peak current than both Ni-Al LDHs/GCE and Gr/GCE, indicating the high extraction capability and excellent electron transfer ability of Ni-Al LDHs/Gr composites towards MP.

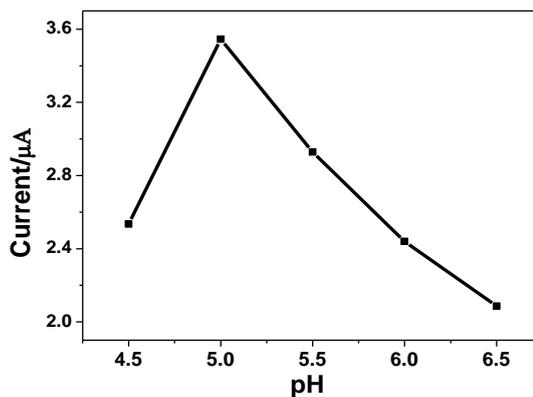


**Figure 3.** SWVs of Ni-Al LDHs/GCE (a), Gr/GCE (b), Ni-Al LDHs/Gr/GCE (c) in 0.1 M ABS (pH 5.0) after preconcentration of 2  $\mu\text{g/mL}$  MP for 10 min.

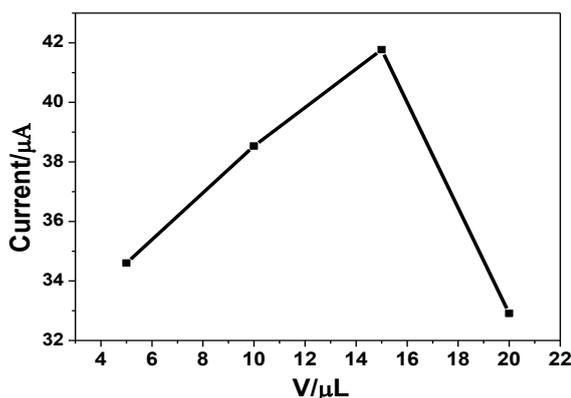
### 3.3. Optimization of experimental parameters for MP analysis

The experimental parameters were optimized to achieve a highly sensitive analysis of MP. Fig. 4 shows effect of the pH value of the electrolyte solution on the SWV responses of MP captured Ni-Al LDHs/Gr/GCE. It was found that the SWV response increased with an increase of pH up to 5.0, but decreased at higher pH. This is probably attributed to the fact that MP would be degraded in the basic media and meanwhile  $\text{H}^+$  participated in the irreversible reduction of MP [5]. Thus, pH 5.0 was chosen for measurements in this work.

Fig. 5 shows the influence of the dropped volume of Ni-Al LDHs/Gr suspension on the SWV response of MP captured Ni-Al LDHs/Gr/GCE. The SWV response was firstly enhanced with the increased volume of Ni-Al LDHs/Gr suspension and then decreased with its further increase. A maximum peak current was obtained when 15  $\mu\text{L}$  of Ni-Al LDHs/Gr suspension was dropped onto electrode surface. Therefore, 15  $\mu\text{L}$  was used in the subsequent experiment.

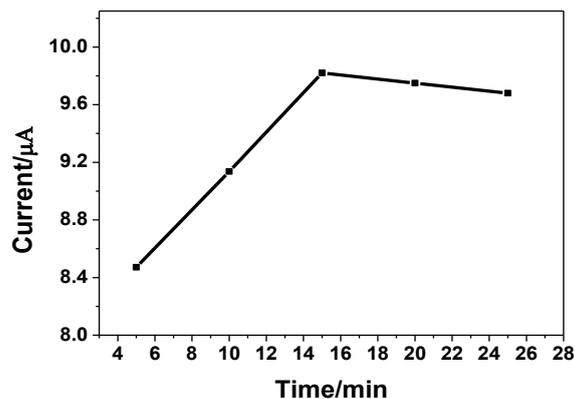


**Figure 4.** Effect of the pH value of the electrolyte solution on the SWV response of MP captured Ni-Al LDHs/Gr/GCE. Other conditions are the same as Fig.3.



**Figure 5.** Effect of the dropped volume of Ni-Al LDHs/Gr suspension on the SWV response of MP captured Ni-Al LDHs/Gr/GCE. Other conditions are the same as Fig.3.

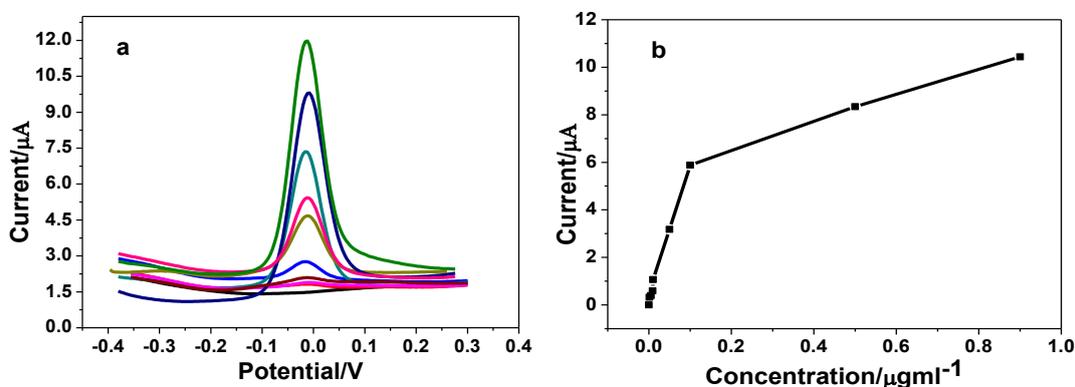
Fig. 6 shows the influence of the preconcentration time on the SWV response of MP captured Ni-Al LDHs/Gr/GCE. As observed, the SWV response was gradually enhanced with an increase of preconcentration time, and then tended to be stable at 15 min. This suggests that the adsorption equilibrium and saturation was reached. Thus, 15 min of preconcentration time was employed.



**Figure 6.** Influence of the preconcentration time on the SWV response of MP captured Ni-Al LDHs/Gr/GCE. Other conditions are the same as Fig.3.

### 3.4. Analytical performance for the detection of MP

Fig. 7a presents the SWV signals of adsorbed MP by different concentration at Ni-Al LDHs/Gr/GCE. As can be seen, well-shaped peak currents were obviously enhanced with the increase of MP concentration. Two linear relationships were obtained in the concentration range of 0-0.1 and 0.1-0.9  $\mu\text{g mL}^{-1}$  (Fig. 7b). The linear regression equations can be expressed as  $I(\mu\text{A})=0.16371+60.92964 C (\mu\text{g mL}^{-1})$  and  $I(\mu\text{A})= 5.37279+ 5.69375 C (\mu\text{g.mL}^{-1})$ , with the correlation coefficients of 0.9988 and 0.9979, respectively. The detection limit is estimated to be 0.6  $\text{ng mL}^{-1}$  ( $S/N=3$ ). Comparison with other modified electrode, the present Ni-Al LDHs/Gr/GCE exhibits the wider linear range and lower detection limit for MP detection (Table 1). Therefore, the developed Ni-Al LDHs/Gr composite is reliable for quantitative analysis of MP.

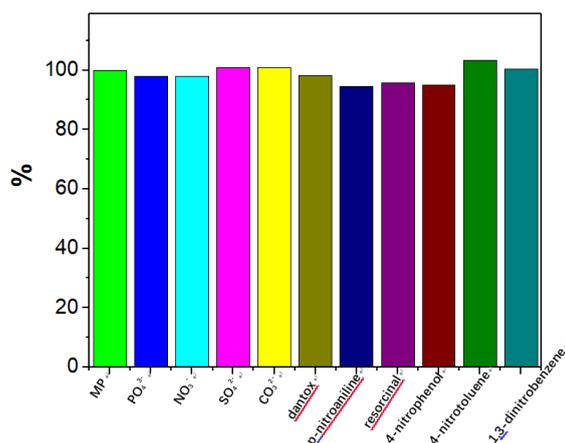


**Figure 7.** (a) SWV signals of increasing MP concentrations (from bottom to top, 0, 1, 5, 9, 10, 50, 100, 500, and 900  $\text{ng mL}^{-1}$ , respectively) and (b) the obtained calibration curve. Other conditions are the same as Fig.3.

**Table 1.** Comparison of the analytical performance of other reported modified electrodes toward MP detection.

electrodes	technique	linear range ( $\mu\text{g mL}^{-1}$ )	LOD ( $\text{ng mL}^{-1}$ )	reference
PEDOT/YSZ@rGO/SS	SWV	0.005-4	1.57	17
CuO-NPs/AC/GCE	DPV	0.05-1.5	2.42	18
Zr(IV)-MDPA-Au	SWV	0.001-0.18	0.2222	19
Au-ZrO <sub>2</sub> -GNs/GCE	SWV	0.001-2.4	1	20
Ni-Al LDHs/Gr/GCE	SWV	0-0.1 0.1-0.9	0.6	This work

Anti-interference ability is an important factor for evaluating an electrochemical MP sensor, because some inorganic ions and other organic species even pesticides are always contained in real sample. As shown in Fig. 8, SWV response of  $2 \mu\text{g mL}^{-1}$  MP were performed in the solutions with the presence of 50-fold excess of  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and 5-fold excess of dantox, p-nitroaniline, resorcinol, 4-nitrophenol, 4-nitrotoluene, 1,3-dinitrobenzene, respectively. It can be found that no obvious interferences observed because the peak currents of MP varied slightly in the presence of the above interferences, indicating good selectivity of the present method for detection of MP. The freshly prepared Ni-Al LDHs/Gr/GCE was stored at  $4^\circ\text{C}$  in a dry condition when it was not used. In the first 5 days storage, there was no distinct change for the SWV response of MP. After a month storage, the Ni-Al LDHs/Gr/GCE still retained 93% of its initial current response. These results show an excellent stability of the present sensor.

**Figure 8.** Interference studies of Ni-Al LDHs/Gr/GCE for detection of MP. Experiments were carried out by recording SWV peak currents of  $2 \mu\text{g mL}^{-1}$  MP in the absence and presence of 0.1 M of  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and  $10 \mu\text{g mL}^{-1}$  of dantox, p-nitroaniline, resorcinol, 4-nitrophenol, 4-nitrotoluene, 1,3-dinitrobenzene. The influence was expressed by the ratio of the peak currents of MP in the presence of interferences and the peak current with only MP contained.

### 3.5. Real sample analysis

To demonstrate the feasibility of Ni-Al LDHs/Gr/GCE for detection of MP in real samples, cabbage from the local market was used. There was no MP detected in cabbage samples. Thus, three cabbage samples spiked with 200.0, 500.0 and 800.0 ng mL<sup>-1</sup> MP were prepared for analysis. As displayed in Table 2, the recoveries of MP in these samples were 98.6–100.9 % with RSD of 2.7–4.1%.

**Table 2.** Comparison of the analytical performance of other reported modified electrodes toward MP detection.

samples	C <sub>added</sub> (ng mL <sup>-1</sup> )	C <sub>measured</sub> (ng mL <sup>-1</sup> )	RSD (%)	Recovery (%)
1	200.0	197.3	3.5	98.6
2	500.0	504.6	2.7	100.9
3	800.0	792.1	4.1	99.0

## 4. CONCLUSIONS

In summary, Ni-Al LDHs/Gr composites were synthesized through a one-step coprecipitation method. The unique nanosheet structure, large surface area, good electron transfer ability and high enrichment effect introduced by Ni-Al LDHs/Gr makes the composites fascinating materials for solid-phase extraction of analyte and electrochemical detection. The results demonstrated that the Ni-Al LDHs/Gr composites exhibit high performance for sensitive and selective determination of MP. Two linear range (0-0.1 and 0.1-0.9 μg mL<sup>-1</sup>) and very low detection limit (0.6 ng mL<sup>-1</sup>) of MP were obtained. Common inorganic ions and organic species did not interfere with the determination of MP. This work offered a reliable and feasible method for electrochemical detection of OPs.

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