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One-step fabrication of layered double hydroxides/graphene hybrid as solid-phase extraction for stripping voltammetric detection of methyl parathion

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ABSTRACT

We developed a green and facile electrochemical approach to synthesize novel Ni/Al layered double hydroxides decorated graphene nanosheets hybrid (labeled as LDHs-GNs) on a cathodic substrate. The as-prepared LDHs-GNs composite is highly efficient to capture organophosphate pesticides (OPs), combining the advantages of LDHs (high enrichment capability for OPs by a selective intercalation) together with GNs (large surface area and high conductivity). It dramatically facilitates the enrichment of OPs onto their surface and realizes the sensitive stripping voltammetric detection of methyl parathion (MP) as a model of OPs. The detection limit for MP in aqueous solutions was determined to be of 0.6 ng mL^{-1} (S/N = 3). This work provides a green and facile route for the preparation of GN-based hybrid, and also offers a new promising protocol for OP analysis.

1. Introduction

Graphene nanosheets (GNs), a perfect two-dimensional (2D) carbon material found in 2004, have attracted tremendous attention [1,2], due to its novel properties, such as exceptional thermal and mechanical properties, high surface areas (calculated value, 2630 m^2/g), and high electrical conductivity. To combine well unique properties of individual nanostructures, recently, GN-based hybrids, as a multifunctional assembly, have been highly concerned in sensing applications [3–7]. For example, various GN-based hybrids, including GNs combined with metal nanoparticles (NPs), metallic oxide NPs, or cyclodextrin, etc., have been fabricated as enhanced electrochemical sensing platforms [5–9]. It has been demonstrated that GN-based hybrids as sensing platforms display extraordinary activity. Currently, how to construct a high-performance GN-based sensing platform in a simple, green and controllable fashion has become a key issue.

To date, GN-based hybrids are primarily prepared by the chemical reduction of exfoliated graphite oxide (GO) combined with chemical precipitation [2,3,10], always involved with chemical reduction process. Nevertheless, the excessive amounts of reducing agents employed may contaminate the resulting materials; a large amount of framework defects is inevitable to be produced, and then the produced defects would severely impair the conductivity of the reduced GNs [11]. These severely restrict the further applications of GNs. Recently, Xia et al. proposed a green and fast approach by in situ electrochemical reduction of exfoliated GO into GNs [12]. More recently, our group further developed a facile co-electrodeposition approach to synthesize ZrO_2NPs-decorated GNs hybrid coating [13]. Obviously, this approach has several clear advantages: no toxic solvents are used and therefore will not result in contamination of the product; the high negative potential used can overcome the energy barriers for the complete reduction; and the final solid film of GNs can be further used in sensor [12]. In particular, the co-electrodeposition provides an effective strategy for nanofabrication by deliberately introducing the functional building block into the assembly. Recently, as a typical class of two-dimensional layered anionic clays, layered double hydroxides (LDHs) have received much attention as host materials to construct functional host-guest materials [14–19]. Previous studies on the adsorption of some hazardous organic molecules have shown that the phenolic compounds or pesticides could be selectively intercalated into the interlayer space of LDHs [16–19]. We recently further demonstrated the feasibility for electrochemical stripping analysis of OPs using LDHs as the host of OPs [20,21]. More conveniently, a nanostructured Ni/Al LDHs film could be electrosynthesized at bare glassy carbon surface [14,20]. Inspired by this, we first propose a facile one-step electrodeposition approach to construct nanostructured LDHs-decorated GNs hybrid coating on a glassy carbon electrode (labeled as LDHs-GNs/GCE), without involving the chemical reduction of GO.

The resulting LDHs-GNs composite, combining the individual properties of GNs (large surface area and high conductivity) together with nanostructured LDHs (high enrichment capability for OPs by a selective intercalation process) is believed to be a promising capture of OPs. Recently, solid phase extraction (SPE) of OPs based electrochemical sensors, combining stripping voltammetry has shown to be a highly sensitive technology [5,10,21–23]. It is expected that the

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resulting LDHs-GNs composite could dramatically facilitate the enrichment of OPs, effectively accelerate the electron transfer and realize their rapid, stable and sensitive stripping voltammetric detection. To the best of our knowledge, this is the first report on one-step fabrication of LDHs-GNs hybrid and further utilizing LDHs-GNs composite as a capture for stripping analysis of nitroaromatic OPs.

2. Experimental

2.1. Apparatus

Electrochemical measurement was performed on CHI 660D electrochemical workstation (CHI, USA) with a conventional three-electrode system comprising a platinum wire as an auxiliary electrode, a saturated calomel electrode (SCE) as reference, and the modified or unmodified glass carbon electrode (GCE) as a working electrode. The general morphology of the products was characterized by the scanning electron microscopy (SEM, JSM-5600).

2.2. Reagents

Methyl parathion (MP) was obtained from Treechem Co (Shanghai, China). The Ni/Al-LDHs were electrosynthesized starting from freshly prepared solution of Ni and Al nitrates. All other chemicals were of analytical-reagent grade and used without further purification. Doubly distilled water was used. The 0.1 M phosphate buffer solutions (PBS) of different pH values were prepared for use. All experiments were carried out at ambient temperature.

2.3. Preparation of the modified electrode

Prior to modification, the basal GCE was polished to a mirror finish using 1.0, 0.3 and 0.05 μm alumina slurries. After each polishing, the electrode was sonicated in ethanol and doubly distilled water for 5 min, successively, in order to remove any adsorbed substances. Finally, it was dried under nitrogen atmosphere ready for use. Graphite oxide was synthesized from graphite by a modified Hummers method [24,25]. 10 μL of the resulting graphite oxide dispersion was dropped onto the surface of the cleaned GCE and was kept at room temperature till dry (labeled as GO/GCE). LDHs decorated GNs modified electrode (labeled as LDHs-GNs/GCE) was prepared by immersing the exfoliated GO/GCE into an 0.3 M KNO_3 solution containing 22.5 mM $Ni(NO_3)_2$ and 7.5 mM $Al(NO_3)_2$, and then cycling the potential between 0.1 and −1.4 V (versus SCE) at a scan rate of 50 mV/s for 8 cycles. For comparison, the modification of GNs or Ni/Al-LDHs alone onto GCE was prepared, respectively. To obtain GNs/GCE, according to the previous report [12], the exfoliated GO/GCE was immersed into an aqueous electrolyte of 0.1 M KNO_3 by cycling the potential between 0.1 and −1.4 V (versus SCE) at a scan rate of 50 mV/s for 8 cycles, while Ni/Al-LDHs modified GCE (LDHs/GCE) was also prepared by cycling the potential for 8 cycles in the freshly prepared solutions of Ni and Al nitrates. The as-prepared GNs/GCE, LDHs/GCE, and LDHs-GNs/GCE were rinsed with water and dried at room temperature for further experiments, respectively.

2.4. Measurement procedure

The LDHs-GNs/GCE was first immersed into a stirred sample solution containing the desired MP concentration for a given time, and rinsed with water. Then, it was transferred into the blank electrolyte (0.1 M, pH 5.7 PBS) for SWV measurements. Multiple successive SWV scanning was used to remove the bound MP until the anodic stripping respond disappeared. Also, the regeneration of the sensor surface was achieved.

3. Results and discussion

3.1. Cyclic voltammetric responses and characterizations of the modified electrodes

Fig. 1A illustrates the comparison between the cyclic voltammetric responses for the formation processes of GNs, LDHs and LDHs-GNs on the GCE. The cyclic voltammograms of an exfoliated GO/GCE in a potential range from 0.1 to −1.4 V show a large cathodic current peak at around −1.23 V vs. SCE (curve a) with a starting potential of −0.87 V vs. SCE. This reduction peak could be due to the reduction of the surface oxygen groups at GO, indicating that the exfoliated GO could indeed be reduced electrochemically to form GNs/GCE, agreeing well with the previous report [12]. A typical CV curve for the formation of LDHs/GCE is recorded in freshly prepared solutions of Ni and Al nitrates (curve b). The irreversible peak around −1.11 V vs. SCE could be attributed to the redox behavior of NO_3^-, leading to the formation of LDHs on the bare GCE [14,20]. Interestingly, with the exfoliated GO/GCE immersed into the freshly prepared solutions of Ni and Al nitrates, the general features of the CV curve obtained (curve c) nicely combine the characteristic of the respective CV curves of a and b (Fig. 1A). The obvious cathodic peaks around −1.08 V and −1.29 V (vs. SCE) are believed to correspond to the electrochemical formation of GNs and LDHs, respectively, indicating that LDHs decorated GNs composite coating has been successfully synthesized onto the surface of GCE via this facile electrochemical approach.

The capability of electron transfer of different electrodes was investigated by electrochemical impedance spectra (EIS), shown in Fig. 1B. It can be seen that EIS of the bare GCE 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 modification of the exfoliated GO onto GCE, the semicircle dramatically increases as compared to the bare GCE, suggesting that the exfoliated GO, as an insulating layer, makes the interfacial charge transfer difficult (curve b). After the exfoliated GO film is electrochemically reduced on GCE (GNs/GCE), the semicircles decrease distinctively, even smaller than bare GCE, indicating that the presence of GNs has accelerated electron transfer between the electrochemical probe of $[Fe(CN)_6]^{3-/4-}$ and the electrode (curve c). With the modification of LDHs-GNs/GCE, the EIS obtained is very similar to that of GNs/GCE, indicating that the introduction of LDHs into the composite remained unchanged for the interfacial charge transfer (curve d).

Typical SEM images of the as-synthesized GNs and LDHs-GNs were shown in Fig. 1C and D, respectively. The as-synthesized graphene shows 2D nanosheet morphologies, exhibiting a few thin wrinkles onto the surface, agreeing well with the previous result [12,13]. With the co-electrodeposition of LDHs-GNs, uniform LDHs nanoparticles of ~30 nm in average diameter formed randomly on the sheet (Fig. 1D). Obviously, it further indicates that the co-electrodeposition approach is feasible to form LDHs-GNs hybrid coating.

As known, the effective surface area is a crucial factor influencing the enrichment capability of the target and the electrochemical response. Fig. 2A depicts the chronocoulometric curves at different electrodes for the reduction of 0.5 mM $K_3Fe(CN)_6$. According to equation: $Q = (2nFAD_0^{1/2}\pi^{-1/2}C_0)t^{1/2}$ [13], the sequence of the values of A (surface area) for different electrode is LDHs-GNs/GCE (curve c, 0.58 cm^2) > GNs/GCE (curve b, 0.39 cm^2) > bare GC (curve a, 0.062 cm^2). Obviously, the modification of LDHs-GNs greatly enhances the active area of the surface, which is considerably important for sensing applications.

3.2. Analytical performance for the detection of methyl parathion

Fig. 2B displays the SWV response of adsorbed MP by the SPE process at LDHs-GNs/GCE. Well-defined peaks, proportional to the