

Electrochemistry and Determination of 1-Naphthylacetic Acid Using an Acetylene Black Film Modified Electrode

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The acetylene black (AB) was dispersed into water in the presence of dihexadecyl hydrogen phosphate (DHP) *via* ultrasonication, resulting in a stable and well-distributed AB/DHP suspension. After evaporation of water, an AB/DHP composite film-modified electrode was prepared. The electrochemical responses of $K_3[Fe(CN)_6]$ at the unmodified electrode, DHP film-modified electrode and AB/DHP film-modified electrode were investigated. It is found that the AB/DHP film-modified electrode possesses larger surface area and electron transfer rate constant. Furthermore, the electrochemical behaviors of 1-naphthylacetic acid (NAA) were examined. At the AB/DHP film-modified electrode, the oxidation peak current of NAA remarkably increases. Based on this, a sensitive and convenient electrochemical method was proposed for the determination of NAA. The linear range is in the range from 4.0×10^{-8} to 5.0×10^{-6} mol L⁻¹, and the detection limit is 1.0×10^{-8} mol L⁻¹. Finally, this new sensing method was employed to determine NAA in several soil samples.

Key Words : Acetylene black (AB), Film modified electrode, 1-Naphthylacetic acid (NAA), Determination

Introduction

Acetylene black (AB) is a special kind of carbon black with many fascinating properties such as excellent electric conductivity, large surface area, strong adsorptive ability and porous structure. Until now, AB was extensively used in electrochemistry for various purposes such as electric double-layer capacitor,¹ rapid discharge,^{2,3} cell cathode⁴ and highly-sensitive determination for sodium nitroprusside,⁵ kojic acid,⁶ Pb²⁺,⁷ 2-chlorophenol,⁸ colchicine,⁹ adrenaline¹⁰ as well as 6-benzylaminopurine (6-BAP).¹¹ However, to the best of our knowledge, the application of AB film electrode in the sensitive determination of 1-naphthylacetic acid has not been reported.

1-Naphthylacetic acid (NAA) is naphthalene derivatives extensively used as plant growth regulators and fungicide on fruits. Consequently, trace amounts in soil may be expected coming from agricultural manipulations. To date, different methods such as spectrofluorimetry,^{12,13} phosphorimetry,^{14,15} high-performance liquid chromatography (HPLC)¹⁶ and electrochemistry¹⁷ were reported for the determination of NAA. Herein, we wish to develop a new electrochemical method with high sensitivity, rapid response, good accuracy and low cost for the determination of NAA utilizing the excellent properties of AB. Therefore, the insoluble AB was firstly suspended into water in the presence of a special type of surfactant: dihexadecyl hydrogen phosphate (DHP). *Via* continuous ultrasonication, a stable and well-distributed AB/DHP suspension was obtained. After that, an AB/DHP film-coated electrode was prepared after evaporating the water. The electrochemical behaviors of NAA at the unmodified electrode, DHP film-modified electrode and AB/DHP film-modified electrode were investigated in detail. From the comparisons, it is very clear that the oxidation peak current

of NAA greatly increases, and the oxidation peak potential shifts negatively by 100 mV at the AB/DHP film-modified electrode. These phenomena indicate that the AB/DHP film-modified electrode can remarkably improve the determining sensitivity of NAA.

Experimental

Reagents. All reagents were of analytical grade and used directly. 1.00×10^{-2} mol L⁻¹ stock solution of NAA was prepared by dissolving NAA (Sigma) into ethanol. Working solutions were prepared by appropriate dilutions with ethanol. Acetylene black (purity > 99.99%) was purchased from STREM Chemicals (USA). Dihexadecyl hydrogen phosphate (DHP) was purchased from Fluka (Fluka chime AG, Buchs).

Instruments. All the electrochemical measurements were carried out using a CHI 830B Workstation (CH Instruments, USA). A conventional three-electrode system, consisting of an AB film modified glassy carbon working electrode, a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode, was employed.

Preparation of AB film-modified electrode. 10.0 mg of AB and 10.0 mg DHP were added into 10.0 mL of re-distilled water, and then sonicated for 30 min, resulting in a black and homogeneous AB/DHP suspension. Prior to coating, the glassy carbon electrode (GCE, 3 mm in diameter) was polished with 0.05 μ m aluminum slurry, rinsed thoroughly with re-distilled water and finally sonicated in re-distilled water for 2 min. After that, 10.0 μ L of AB/DHP suspension was added on the clean GCE surface and dried under an IR lamp. The DHP film-modified GCE was prepared by the same procedure as explained above, but without AB.

Analytical procedure. Unless otherwise stated, pH 3.6

HAc-NaAc buffer (0.1 mol L^{-1}) was used as the supporting electrolyte for NAA determination. The accumulation step was carried out under open-circuit while stirring the solution for 5 min. After that, the differential pulse voltammograms from 0.50 to 1.20 V were recorded after 10-s quiescence, and the peak current at 1.06 V was measured for NAA.

Results and Discussion

Electrochemical properties of AB/DHP film-modified GCE. The electrochemical properties of AB/DHP film-modified GCE were investigated using $\text{K}_3[\text{Fe}(\text{CN})_6]$ as electrochemical probe. Figure 1 shows the cyclic voltammograms of $5.0 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$ in $1.0 \text{ mol L}^{-1} \text{ KCl}$ solution at the unmodified GCE, DHP film-modified GCE and AB/DHP film-modified GCE. At the unmodified GCE (curve a), a pair of redox peak is observed for $\text{K}_3[\text{Fe}(\text{CN})_6]$. However, the peak currents obviously decrease at the DHP film-modified GCE (curve b). DHP can form a perfect film on GCE surface and blocks the electron transfer of $\text{K}_3[\text{Fe}(\text{CN})_6]$. Thus, the peak currents show remarkable decline. At the AB/DHP film-modified GCE (curve c), the oxidation and reduction peak currents greatly increase compared with those at the unmodified GCE and DHP film-modified GCE. Furthermore, the electrochemical responses of $\text{K}_3[\text{Fe}(\text{CN})_6]$ under different scan rates were examined. It is found that the peak currents is proportional to the square root of scan rate, suggesting that the electrode process of $\text{K}_3[\text{Fe}(\text{CN})_6]$ is diffusion control. According to the Randles-Sevcik equation, higher peak current means larger surface area. Otherwise, the oxidation peak potential (E_{pa}) shifts negatively and the reduction peak potential (E_{pc}) shifts positively at the AB/DHP film-modified electrode. So, the peak potential separation lowers, indicating that the electrode process of $\text{K}_3[\text{Fe}(\text{CN})_6]$ becomes more reversible and the AB/DHP film-modified GCE possesses larger standard heterogeneous rate constant. In conclusion, the AB/DHP film-modified GCE exhibits unique electrochemical properties, compared with DHP film-modified GCE and unmodified GCE.

Electrochemical behavior of NAA. The electrochemical

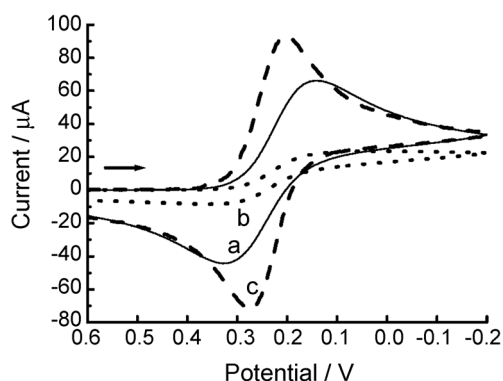


Figure 1. Cyclic voltammograms of $\text{K}_3[\text{Fe}(\text{CN})_6]$ at bare GCE (curve a), DHP film-modified GCE (curve b) and AB/DHP film-modified GCE (curve c).

responses of NAA at the unmodified GCE, DHP film-modified GCE and AB/DHP film-modified GCE were examined in various supporting electrolytes such as $0.01 \text{ mol L}^{-1} \text{ HClO}_4$, pH 3.6, 4.0, 4.6, 5.0, 5.6 HAc-NaAc buffer (0.1 mol L^{-1}), pH 6.0, 7.0, 8.0 phosphate buffer (0.1 mol L^{-1}). In pH 3.6 HAc-NaAc buffer, the cyclic voltammetric signals of NAA is relatively better since the oxidation peak shape is best-defined and the peak current is highest. Thus, the electrochemistry and determination of NAA was studied in pH 3.6 HAc-NaAc buffer.

Figure 2 shows the cyclic voltammograms of $1.0 \times 10^{-5} \text{ mol L}^{-1}$ NAA in pH 3.6 HAc-NaAc buffer at different working electrodes. At the unmodified GCE (curve a), only an oxidation peak is observed at 1.16 V for NAA during the cyclic sweep between 0.00 V and 1.30 V. At the DHP film-modified GCE (curve b), the i_{pa} of NAA decreases by about 50%, and the oxidation peak potential (E_{pa}) shifts positively. The DHP film on GCE surface is perfect and has poor electric conductivity. So, the mass transport and electron transfer of NAA at the DHP film-modified GCE becomes difficult, resulting in the peak current decline and positive shift of E_{pa} . However, the electrochemical responses of NAA at the AB/DHP film-modified GCE (curve c) are quite different from those at unmodified and DHP-modified GCEs. It is found that the i_{pa} of NAA remarkably increases and the E_{pa} shifts negatively at the AB/DHP film-modified GCE. AB possesses large surface area and strong adsorptive ability, therefore, the AB/DHP film modified GCE shows higher accumulation efficiency toward NAA, resulting in remarkable peak current enhancement. Additionally, the cyclic voltammograms of AB/DHP film-modified GCE in pH 3.6 HAc-NaAc buffer without NAA are shown in curve (d) for better comparison, and no redox peaks are observed. In brief, it is very clear that the AB/DHP film-modified electrode significantly increases the determining sensitivity of NAA because of its unique properties.

Effect of scan rate. The influence of scan rate on the oxidation peak current of NAA at the AB/DHP film-modified GCE was investigated by LSV. As scan rate increasing from 25 to 300 mV s^{-1} , the oxidation peak current of NAA

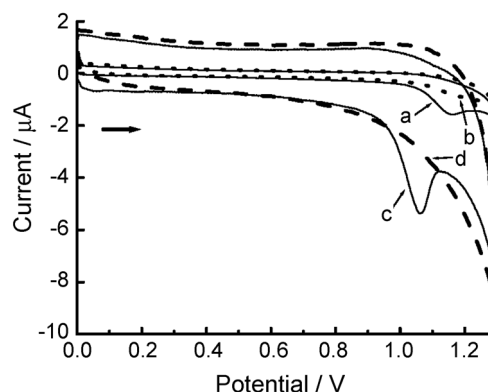


Figure 2. Cyclic voltammograms of $1.0 \times 10^{-5} \text{ mol L}^{-1}$ NAA in pH 3.6 HAc-NaAc buffer at bare GCE (a), DHP film-modified GCE (b) and AB/DHP film-modified GCE (c). (d): Cyclic voltammograms of AB/DHP film-modified GCE in pH 3.6 buffer.

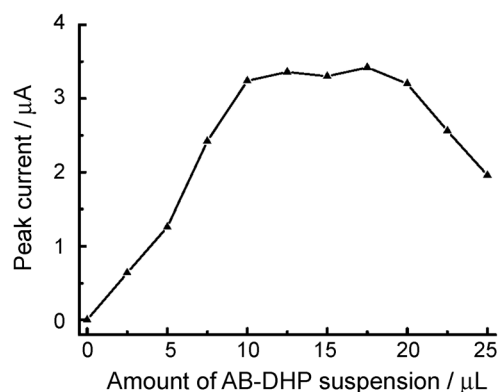


Figure 3. Effect of the amount of AB/DHP suspension on the oxidation peak current of $1.0 \times 10^{-6} \text{ mol L}^{-1}$ NAA.

increases linearly, revealing that the oxidation of NAA at the AB/DHP film-modified GCE is controlled by adsorption.

The amount of AB/DHP suspension. The effect of amount of AB/DHP suspension that used to modify GCE surface was examined. Figure 3 demonstrates the variation of oxidation peak current of NAA as a function of the amount of the AB/DHP suspension. As the amount of AB/DHP suspension increases from 0 to 10.0 μL , the oxidation peak current increases remarkably. However, the oxidation peak current increases slightly as further improving the volume of AB/DHP suspension to 20.0 μL . If the amount of AB/DHP suspension exceeds 20.0 μL , the oxidation peak current conversely decreases. DHP has low electronic conductivity and can block the mass transport of NAA. So the oxidation peak current of NAA conversely decreases when the amount of AB/DHP suspension is too much. In order to shorten the time that consumed to evaporate water and achieve high sensitivity, 10.0 μL of AB/DHP suspension was used to modify electrode.

Accumulation time. Figure 4 illustrates the relationship between the oxidation peak current of NAA and the accumulation time. When the accumulation time improves from 0.0 to 5.0 min, the oxidation peak current of $1.0 \times 10^{-6} \text{ mol L}^{-1}$ of NAA gradually increases at the AB/DHP film-modified GCE. As extending accumulation time, the amount of NAA that accumulated at AB film surface also increases. Without a doubt, the oxidation peak current of NAA increases. However, the oxidation peak current of NAA almost keeps unchanged as the accumulation time is longer than 5.0 min, indicating that the amount of NAA at the AB film surface tends to limiting value. Considering both the sensitivity and the working efficiency, 5.0 min was chosen as the optimal accumulation time.

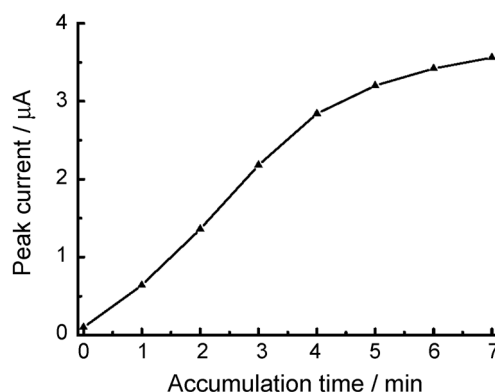


Figure 4. Influence of accumulation time on the oxidation peak current of $1.0 \times 10^{-6} \text{ mol L}^{-1}$ NAA.

Repeatability and reproducibility. The repeatability was evaluated by successive measuring the same $1.0 \times 10^{-6} \text{ mol L}^{-1}$ NAA for 6 times at a single AB/DHP modified electrode. After each measurement, the modified electrode was thoroughly rinsed with water, transferred into the blank electrolyte and scanned for 5 cycles to remove any adsorbates. The relative standard deviation (RSD) of 5.6% indicates excellent repeatability. Additionally, the reproducibility between multiple electrode preparations was estimated by comparing the oxidation peak current of $1.0 \times 10^{-6} \text{ mol L}^{-1}$ NAA. The RSD is 6.2% for 10 AB/DHP modified-GCEs, revealing that the method for preparation of AB/DHP film-modified GCE has good potential applications.

The long-term stability of the AB/DHP film-modified GCE was estimated by measuring the current response at a fixed NAA concentration of $1.0 \times 10^{-6} \text{ mol L}^{-1}$ over a period of 3 weeks. The AB/DHP film-modified GCE was used daily and stored in air. The experimental results show that the current response only deviates 6.4%, suggesting that the AB/DHP film coated GCE possesses long-term stability.

Linear range and limit of detection. The varying of oxidation peak current with concentration was studied using differential pulse voltammetry (DPV). The DPV parameters are: accumulation time = 5 min; pulse amplitude = 50 mV, scan rate = 40 mV s^{-1} , pulse width = 40 ms. It is found that the oxidation peak current of NAA increases linearly with its concentration in the range from 4.0×10^{-8} to $5.0 \times 10^{-6} \text{ mol L}^{-1}$ ($r = 0.998$). Otherwise, the limit of detection was evaluated, and the value is as low as $1.0 \times 10^{-8} \text{ mol L}^{-1}$.

Interference. To evaluate the potential interference of foreign species on the determination of NAA at $1.0 \times 10^{-6} \text{ mol L}^{-1}$, a systematic study was carried out under the above-optimized conditions. The peak currents of NAA in the

Table 1. Interference on the determination of $1.0 \times 10^{-6} \text{ mol L}^{-1}$ NAA

Foreign species	Tolerance level/mol L^{-1}
Ca^{2+} , Mg^{2+} , Fe^{3+} , Zn^{2+} , Al^{3+} , Fe^{3+} , Cu^{2+} , CO_3^{2-} , SO_4^{2-} ,	2.0×10^{-3}
Ascorbic acid, vitamin E, vitamin B6, lysine, phenylalanine, glutamic acid	1.0×10^{-3}
Tryptophane, cysteine, phenol, 2-nitrophenol, 2-aminophenol	5.0×10^{-4}
Indole-3-acetic acid	2.0×10^{-4}

Table 2. Determination of NAA in soil samples

Sample	spectrofluorimetry /ng g ⁻¹	this method /ng g ⁻¹	RSD	Recovery
A	243.1	232.4	4.2%	103.0%
B	156.2	167.5	4.6%	97.5%
C	312.6	315.4	3.9%	99.3%
D	186.4	194.2	4.1%	98.4%
E	302.8	297.4	4.4%	98.9%

absence and presence of foreign species were measured by DPV, and the error was consequently obtained from the peak current change. The results are listed in Table 1. It is found that 2000-fold concentrations of Ca²⁺, Mg²⁺, Fe³⁺, Zn²⁺, Al³⁺, Fe³⁺, Cu²⁺, CO₃²⁻, SO₄²⁻, 1000-fold concentrations of ascorbic acid, vitamin E, vitamin B6, lysine, phenylalanine, glutamic acid, 500-fold concentrations of tryptophane, cysteine, phenol, 2-nitrophenol, 2-aminophenol, and 200-fold concentrations of indole-3-acetic acid, almost do not interfere with the oxidation signal of NAA (error < 10%).

Analytical application. This newly-proposed method was used to detect NAA in several soil samples, which collected from the tea garden of Enshi and treated as follows: 5.0 g of dried soil sample were extracted with 10.0 mL of absolute ethanol under ultrasonic condition for 30 min, then filtered and the filtrate was diluted with absolute ethanol to 15.0 mL, resulting the soil sample solution. The content of NNA in soil sample was determined by the standard addition method, and the results are listed in Table 2. Each sample was determined in triplication, and the RSD is below 5.0%. In order to testify the accuracy of this method, the spectrofluorimetric method described in reference¹³ was also employed to detect the NAA in soil samples. It is found that the results are in good agreement, indicative of good accuracy of this method. In addition, the recovery of NAA was also tested, and the recovery is in the range from 97.5% to 103.0%, also suggesting that this method has good accuracy.

Conclusion

Owing to the unique properties of AB such as large surface area and strong adsorptive ability, the AB film-modified electrode remarkably improves the determining sensitivity of NAA.

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