Electrochemical sensor based on Na$^+$-doped g-C$_3$N$_4$ for detection of phenol

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Abstract.   In this work, a novel and enhanced electrochemical sensor based on Na$^+$-doped g-C$_3$N$_4$ was constructed for the detection of phenol. First, the g-C$_3$N$_4$ was formed through polymerizing melamine under 520°C. And then the Na$^+$-doped g-C$_3$N$_4$ was fabricated by a simple wet chemical method. The electrochemical sensor was constructed by modifying the carbon paper with the resulting Na$^+$-doped g-C$_3$N$_4$. The morphology, chemical compositions and structure of Na$^+$-doped g-C$_3$N$_4$ were characterized by scanning electron microscopy, transmission electronic microscopy, energy-dispersive X-ray detector and X-ray diffraction. The Na$^+$-doped g-C$_3$N$_4$ electrode was used for the cyclic voltammetry and amperometric response detection of phenol in a 0.1 M phosphate buffer (pH 9.0). Under the optimal conditions, the prepared sensor displayed good performance for the electrochemical detection of phenol with a wide linear range of 1–110 μM, as well as low detection limit of 0.23 μM.

Keywords.   g-C$_3$N$_4$; doped; electrochemical sensor; phenol.

1. Introduction

The graphene-like carbon nitride (g-C$_3$N$_4$) has attracted a lot of attention in the areas of electrochemical sensor [1], photocatalysis [2], heterogeneous catalysis [3] and fuel cells [4], due to its unique electronic structure, peculiar thermal stability and low-cost preparation. Owing to the stacked 2D structure of g-C$_3$N$_4$, the C$_3$N$_4$-modified GC electrode exhibited high sensitivity for the simultaneous electrochemical determination of Pb^{2+}, Hg^{2+} and Cu^{2+} in aqueous media [5]. However, the poor conductivity of pure g-C$_3$N$_4$ is always considered as a drawback, restricting the electron transportation and limiting electrochemical performance. Therefore, combination of g-C$_3$N$_4$ with metal nanomaterials was applied to improve the electrocatalytic activity and then, enhance its sensing performance. For instance, the Ag–g-C$_3$N$_4$ nanocomposites were used to construct nonenzymatic electrochemical sensor for detecting H$_2$O$_2$ with high sensitivity and selectivity [6]. Pt, Au and Pd as noble metals also have been used to functionalize g-C$_3$N$_4$ for the applications in the sensing field [7]. Additionally, a strategy for the assembly of graphene on g-C$_3$N$_4$ was also reported with G–g-C$_3$N$_4$ showing high electrochemical activities [8].

Phenols are extensively used in the manufacture of some insecticides, herbicides and pharmaceuticals [9]. Partially, phenolic compounds were released into water and soil environments due to the high frequent utilization in industrial processes. It can accumulate in the human body and lead to harmful effects, such as itch, anemia, faint and cancer at low concentration. The US Environment Protection Agency (EPA) has listed phenolic compounds as a priority pollutant. The toxic characteristics and highly hazardous of phenols require the development of fast, simple, accurate and sensitive analytical methods for its quantification. Many methods have been established to determine phenol, such as gas chromatography (GC), high-performance liquid chromatography (HPLC), high-performance capillary zone electrophoresis, capillary electrophoresis (CE) and electrochemical methods [10–14]. Among them, constructing sensitive electrochemical sensors for the detection of phenols has attracted much attention due to the advantages of fast response, simple operation, low cost, high sensitivity. Recently, an enhanced electrochemical sensor based on Pt nanoparticles modified g-C$_3$N$_4$ was prepared for the detection of phenol [15]. Owing to the combination of the features of Pt nanoparticles and g-C$_3$N$_4$, the electrochemical sensor exhibited high sensitivity, reproducibility and stability. However, researches on electrochemical sensor for detecting phenol based on g-C$_3$N$_4$ are rare. Further exploring the modified g-C$_3$N$_4$ to improve the electrochemical efficiency is still necessary. In this present paper, Na ion doping has been proposed as an effective way to modify g-C$_3$N$_4$. We synthesized

Na^+-doped g-C_3N_4 by a simple wet chemical method at room temperature, and the fabricated Na^+-doped g-C_3N_4 has been applied for the electrochemical detection of phenol. The synthesized modified electrode showed a good sensitivity with a detection limit of 0.23 μM.

2. Experimental

2.1 *Sample preparation*

g-C_3N_4 was formed through the condensation reaction. Typically, 4 g melamine ($C_3N_6H_6$, ≥99%) was put into the crucible in the muffle furnace and then heated to 520°C for 4 h (5°C min^{-1}) in air. After heat treatment, the resultant g-C_3N_4 was collected. Na^+-doped g-C_3N_4 was synthesized *via* a simple wet chemical method. Sixty milligrams of g-C_3N_4 was suspended in 80 ml of deionized water with sonication for 0.5 h. Then, 15, 20, 25 ml of 4 M NaOH was added to the suspension, respectively, and the solution was stirred for 24 h. Na^+-doped g-C_3N_4 was washed using deionized water and absolute ethanol for several times, respectively, and separated by centrifuge. Eventually, the obtained products dried overnight at 80°C, and were named as NC-15, NC-20, NC-25, respectively.

2.2 *Characterization*

Morphology was investigated with field emission scanning electron microscope (FESEM, Hitachi S-4700) and transmission electron microscopy (TEM, Tecnai G2 F30). The crystal structures of Na^+-doped g-C_3N_4 were characterized by an X-ray diffractometer (Thermo ARL SCINTAG X'TRA) with CuKα radiation (λ = 0.154056 nm) and emission current were 40 kV and 40 mA, respectively. The chemical compositions of as-obtained nanocomposites were investigated using an energy-dispersive X-ray detector (EDS, Thermo Noran VANTAG-ESI).

2.3 *Electrochemical measurements*

The as-prepared Na^+-doped g-C_3N_4 (5 mg) was dispersed in dimethyl formamide (DMF, 1.0 ml) and sonicated for 0.5 h to form a homogenous yellow suspension. Five microlitres of the suspension was dripped onto the carbon paper (CP, 0.3 × 0.5 cm^2) surface and dried at room temperature to obtain the working electrode. All electrochemical measurements were carried out using a CHI660C electrochemical workstation with a conventional three-electrode system at room temperature in phosphate buffer solution (PBS) containing different amount of phenol. This system was equipped with the as-prepared Na^+-doped g-C_3N_4 modified CP as the working electrode, a saturated Ag/AgCl electrode as the reference electrode and a platinum wire as the counter electrode.

3. Results and discussion

SEM and TEM images are shown in figure 1 to display the morphology of the as-prepared sample. The Na^+-doped g-C_3N_4 (NC-20) was consisted of solid agglomerates with a size of 1–4 μM (figure 1a). TEM image of Na^+-doped g-C_3N_4 sample is shown in figure 1b, which further confirmed that the prepared sample had irregular cubic morphology. In addition, TEM image of the g-C_3N_4 is also shown in figure 1c. It can be seen from the comparison that the introduction of Na^+ had little effect on the morphology of the g-C_3N_4. To study the chemical composition of Na^+-doped g-C_3N_4 samples, EDS measurement was performed and shown in figure 1d. It can be observed that the surface of the sample contained Na, C and N elements. The weight ratio of Na in Na^+-doped g-C_3N_4 samples of the NC-15, NC-20, NC-25 were calculated to be 2.14, 2.55, 2.72, respectively.

The detailed information on the crystal structure of Na^+-doped g-C_3N_4 samples was obtained by X-ray diffraction (XRD). The XRD patterns of Na^+-doped g-C_3N_4 samples (NC-20) are shown in figure 2. It can be seen that two typical characteristic peaks were observed on the XRD diffractograms of samples, which is consistent with the standard data of bulk g-C_3N_4 (JCPDS 87-1526). The broad and intense peak at $2\theta = 27.5°$ (002) corresponds to the inter-planar stacking interaction of conjugated aromatic systems. The low-angled one at $2\theta = 13.1°$ (100) corresponds to the in-plane trigonal N linkage of tri-s-triazine. It was noteworthy that the peak position of the (200) diffraction peak on Na^+-doped g-C_3N_4 shifted slightly toward a higher 2θ value, indicating that the corresponding interlayer distance was slightly changed due to the Na^+ doping in g-C_3N_4. In general, ion doping will induce changes in the lattice parameters.

To investigate the electrochemical behaviours of the samples CP, g-C_3N_4/CP and Na^+-doped g-C_3N_4/CP electrodes were tested in 0.10 M PBS (pH 3.0) with 50 μM phenol using cyclic voltammetry (CV). Figure 3 showed the results of cyclic voltammograms, which showed no oxidative current on the bare CP electrode. As for the g-C_3N_4/CP electrode, a weak current response was observed at the potential of 0.63 V. However, a significant enhancement in the peak current was obtained when the PC electrode is modified with Na^+-doped g-C_3N_4. The CV results may suggest that the Na^+-doped g-C_3N_4/CP electrode is highly sensitive for the electrochemical detection of phenol. Moreover, the NC-20/PC showed a higher oxidation peak current at potential of 0.63 V.

Figure 4 showed the impedance spectra of g-C_3N_4/CP and Na^+-doped g-C_3N_4/CP electrode in 0.10 M PBS (pH 3.0) containing 50 μM phenol. The semicircle portion of Na^+-doped g-C_3N_4 at higher frequencies is distinctly smaller than that of g-C_3N_4, demonstrating the Na^+ doping introduced the favourable access for the electron transfer on Na^+-doped g-C_3N_4 electrode. The slope of Na^+-doped g-C_3N_4 was also smaller than that of g-C_3N_4, which suggested that
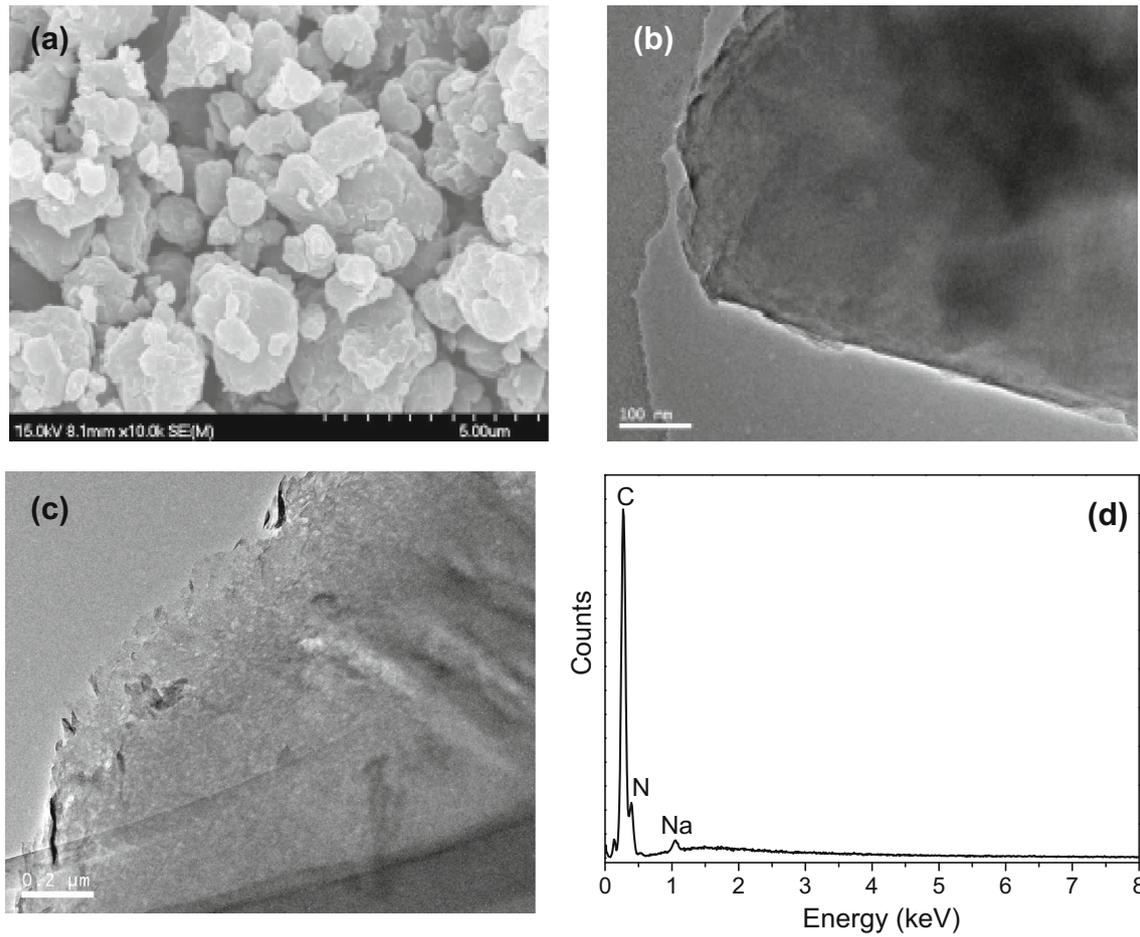
Figure 1. (**a**) SEM and (**b**) TEM images of Na^+-doped g-C_3N_4, (**c**) TEM images of g-C_3N_4 and (**d**) EDS spectrum of Na^+-doped g-C_3N_4.

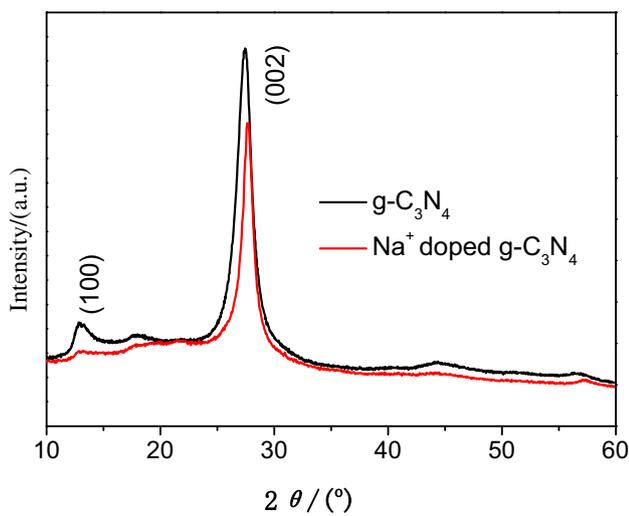**Figure 2.** XRD pattern of g-C_3N_4 and Na^+-doped g-C_3N_4.
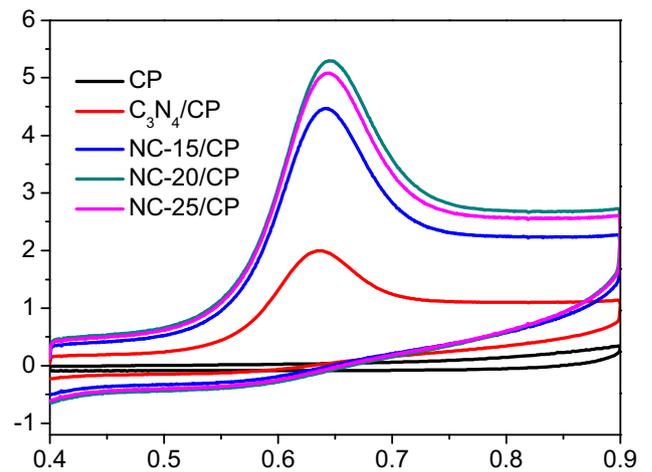
Figure 3. Cyclic voltammetric behaviours of 50 μM phenol at bare CP, g-C_3N_4/CP and Na^+-doped g-C_3N_4/CP in 0.1 M PBS (pH = 9.0) at a scan rate of 100 mV s^{-1}.
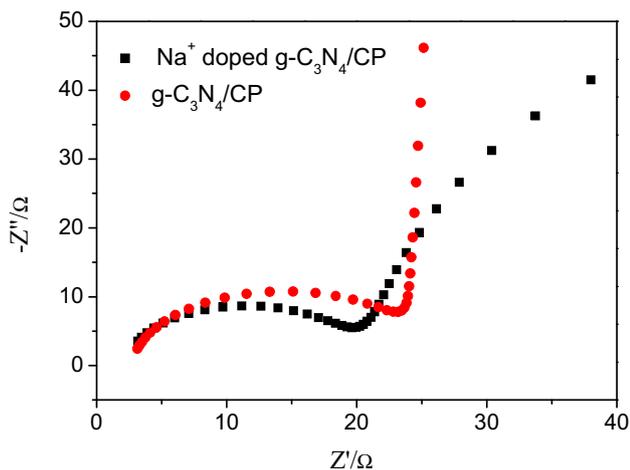
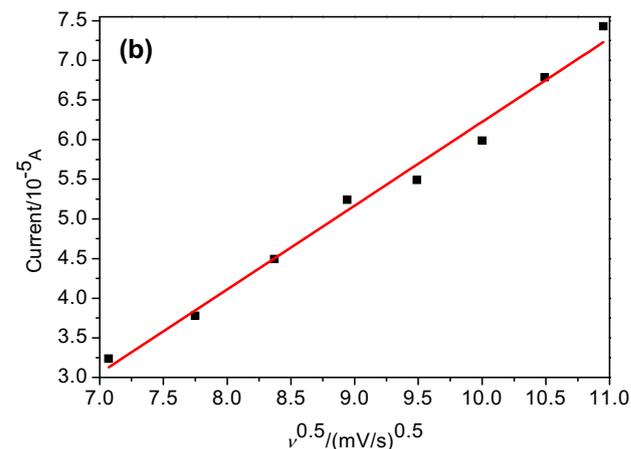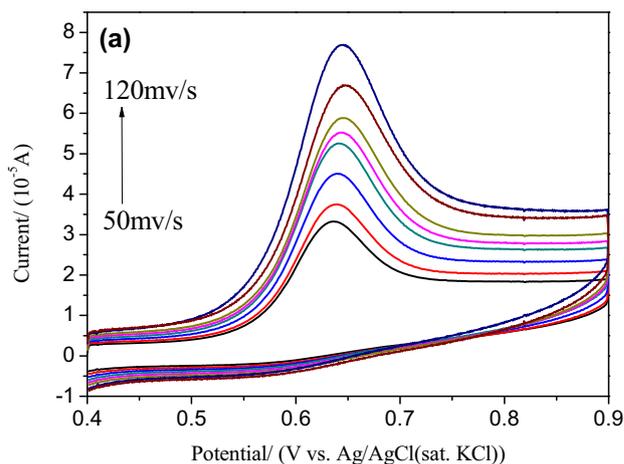**Figure 4.** Electrochemical impedance spectroscopy of g-C$_3$N$_4$ and Na$^+$-doped g-C$_3$N$_4$.
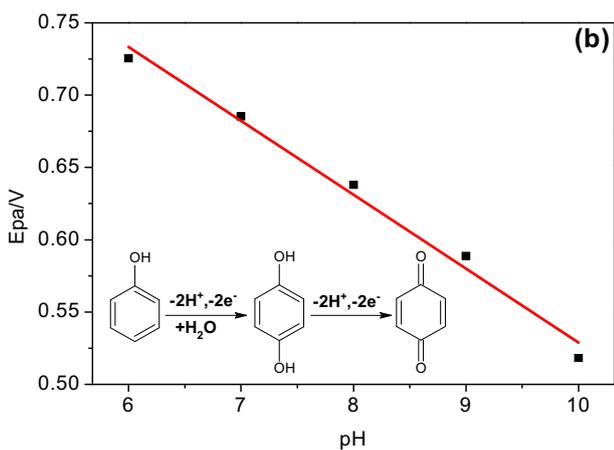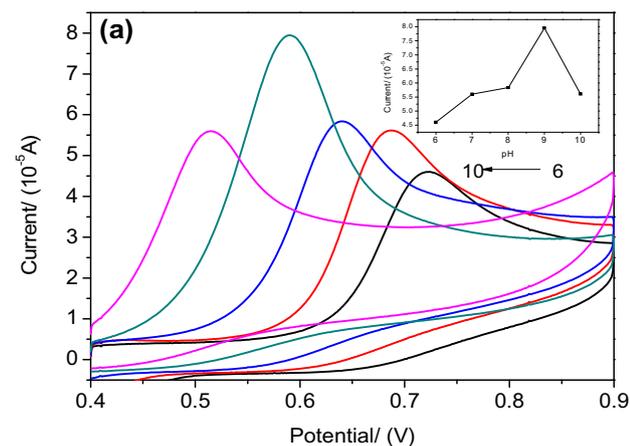

Figure 5. (**a**) Cyclic voltammograms of 50 μM phenol in 0.1 M PBS at the Na$^+$-doped g-C$_3$N$_4$ in different pH (6.0–10.0), the inset shows the relationship between the current response and the pH. (**b**) The linear relationship between pH and peak potential; scan rate 50 mV s^{-1}.

Figure 6. (**a**) CV response of Na$^+$-doped g-C$_3$N$_4$/CP in 0.1 M PBS (pH = 9.0) containing 50 μM phenol at different scan rates from 50 to 120 mV s^{-1}. (**b**) The linear relationship between the oxidation peak current (I_{pa}) and the square root of the scan rate ($v^{1/2}$).

the composite is more conducive to diffusion limited process. Therefore, the improved sensing performance of Na$^+$-doped g-C$_3$N$_4$/CP may be due to excellent electron transfer efficiency and the high specific surface area.

The pH of supporting electrolyte is important factors affecting the electrochemical behaviour of electrodes for electrochemical phenol oxidation. In order to increase the sensitivity of electrochemical determination, CVs of Na$^+$-doped g-C$_3$N$_4$/CP in 0.1 M PBS with 50 μM was investigated in different pH ranging from 6.0 to 10.0, and the results were shown in figure 5a. For the 0.1 M PBS in the pH range of 6.0–10.0, the maximum peak current for phenol oxidation was achieved at pH of 9.0, while the peak potential shifted negatively with pH continued to increase. The maximum peak current was observed at pH lower than the pKa of phenol (pKa = 9.95), which suggested that the non-dissociated form of phenol may be better adsorbed on the Na$^+$-doped g-C$_3$N$_4$/CP surface. Therefore, optimal pH 9.0 would be used in the following experiment. Besides, the relationship between pH in the range
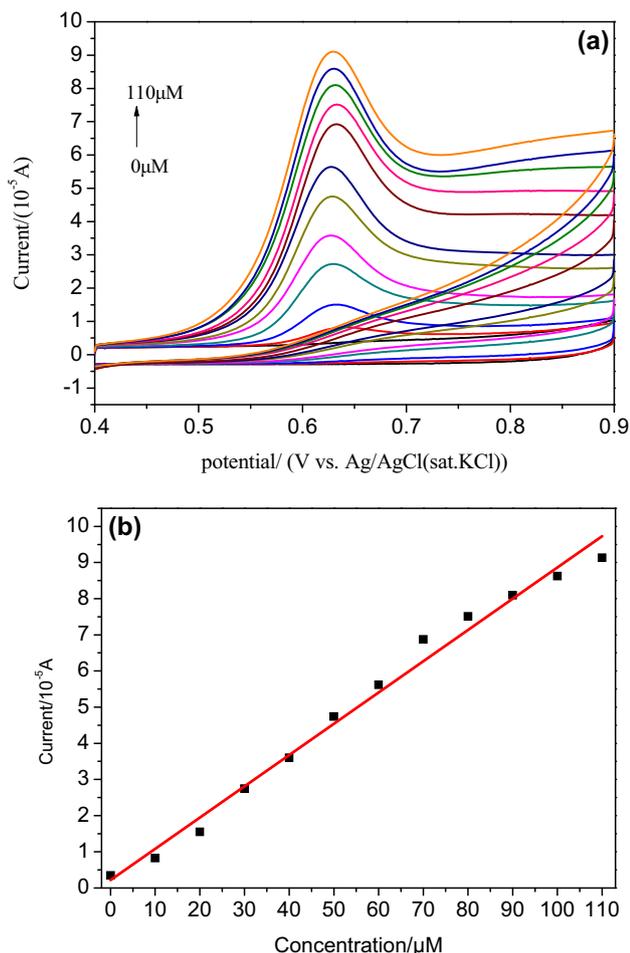
Figure 7. (**a**) CVs of different concentrations of phenol (0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 μM) at Na$^+$-doped g-C$_3$N$_4$/CP in 0.1 M PBS (pH = 9.0) at a scan rate of 100 mV s^{-1}. (**b**) The plot shows the linear relationship between peak current and concentration; scan rate 100 mV s^{-1}.
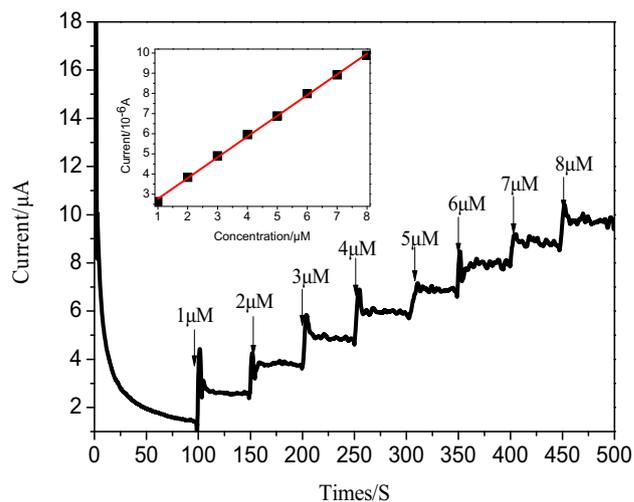

Figure 8. Amperometric response of Na$^+$-doped g-C$_3$N$_4$/CP, the illustration is the calibration curve for the current response and the corresponding concentration.
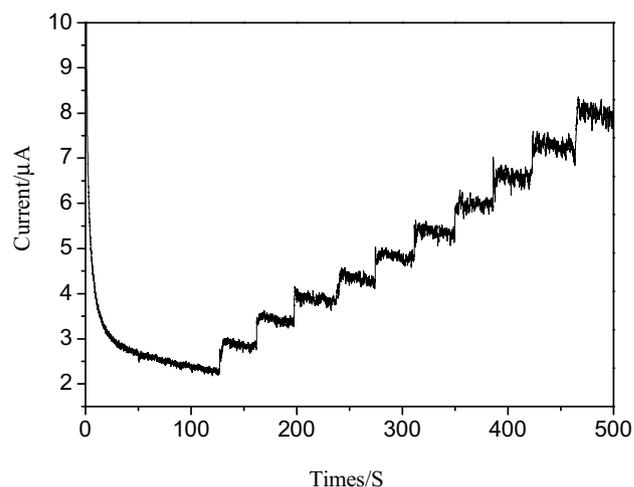

Figure 9. Amperometric response of Na$^+$- doped g-C$_3$N$_4$/CP (the electrode was placed at normal temperature for 7 days before use).

of 6.0–10.0 and the peak potential (E_{pa}) of phenol oxidation was also studied. The regression equation of pH and the E_{pa} was gained: E_{pa} (V) = −0.05109V/pH + 1.040V (R^2 = 0.9783) (figure 5b). The slope is −0.05109V/pH, which was close to the theoretical value (−0.059V/pH) indicating that the same number of protons and electrons were involved in the oxidation process of phenol. Therefore, a possible mechanism is showed in the inset of figure 5b.

To investigate reaction kinetics, the effect of scan rate on the oxidation of phenol was also investigated. Figure 6a showed CVs of 50 μM phenol at Na$^+$-doped g-C$_3$N$_4$/CP with different scan rates. It can be seen that the oxidation peak current increased with increasing scan rate. The anodic peak current (I_{pa}) values exhibited a good linear relationship with the square root of the scan rate ($v^{1/2}$) in the range of 50–120 mV s^{-1}. The regression equation was I_{pa} (10^{-5} A) = 1.056$v^{1/2}$ − 4.342 (R^2 = 0.9750), which indicated that

the electrode reaction of phenol on Na$^+$-doped g-C$_3$N$_4$/CP electrode was a typical diffusion controlled process.

The CV was used for the determination of phenol on Na$^+$-doped g-C$_3$N$_4$/CP electrode in 0.1 M PBS (pH 9.0) solution, at the potential scanning from 0.4 to 0.9 V with the scan rate of 100 mV s^{-1}. As shown in figure 7a, with the increase in the concentration of phenol from 10 to 110 μM, the peak current gradually increased. Under the optimum conditions, the linearity between the peak current and concentration of phenol can be expressed as the equation: I_{pa} (10^{-5} A) = 0.08630C (μM) + 0.2191 (R^2 = 0.9871) (figure 7b).

The amperometric response was employed for the determination of phenol with the Na$^+$-doped g-C$_3$N$_4$/CP electrode, due to its higher current sensitivity and better resolution

than CV at low concentration. Figure 8 represents the typical amperometric response of the Na$^+$-doped g-C$_3$N$_4$/CP electrode upon successive step-wise additions of phenol in a 0.1 M PBS (pH 9.0) at applied potential of 0.65 V. The Na$^+$-doped g-C$_3$N$_4$/CP electrode responded rapidly to phenol, the current reached plateau within 3 s, indicating that electrode has a short response time for the determination of phenol. The Na$^+$-doped g-C$_3$N$_4$/CP electrode showed linear relationship to the phenol concentration (1–8 μM), with regression equation of: I_{pa} (μA) = 1.029C (μM) + 1.743 (R^2 = 0.9987) (figure 8 inset). The low detection limit of phenol sensing was estimated to be 0.23 μM, and sensitivity was calculated as 7.27 μA μM^{-1} cm^{-2}. The amperometric response was also measured on used Na$^+$-doped g-C$_3$N$_4$/CP electrode that was kept at normal condition for 7 days. As can be seen from figure 9, the peak current has not significantly decreased even after 7 days storage, which may demonstrate the long-term stability of the proposed electrode.

4.   Conclusion

In summary, a novel electrochemical sensor based on Na$^+$-doped g-C$_3$N$_4$ for the determination of phenol was developed. The Na$^+$-doped g-C$_3$N$_4$/CP electrode exhibited a higher current response in CV towards phenol oxidation, and it was used for the electrochemical sensitive detection of phenol in 0.1 M PBS (pH 9.0). The linear range of 1 to 110 μM was obtained, while the detection limit was found to be 0.23 μM, and sensitivity was calculated as 7.27 μA μM^{-1} cm^{-2}.

This Na$^+$-doped g-C$_3$N$_4$ electrode explored the potential applications of g-C$_3$N$_4$ for sensors, representing a platform for environment-friendly and designing low toxicity electrochemical sensors.

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