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### Makale Başlığı / Title

A novel Cu(II) detection assay via modified glassy carbon electrode

Modifiye edilmiş camsı karbon ile yeni bir Cu(II) analiz yöntemi

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## Abstract

Copper (Cu(II)) is an essential and necessary micronutrient for many plants and animals at very low levels. However, it is toxic to aquatic plants at high levels due to its association with cell membranes. Glassy carbon electrode (GCE) was modified by the 3-phenyl-4-[2-(2-naphthylsulfonyloxy)-benzylidenamino]-4,5-dihydro-1H-1,2,4-triazol-5-one (3-PNO) in 0.1 M supporting electrolyte. The modified surface was confirmed by cyclic voltammetry (CV) and x-ray photoelectron spectroscopy (XPS). According to characterization data, the GCE with 3-PNO was successfully obtained. The GCE with 3-PNO was utilized for Cu(II) ions analysis in water samples. The concentration range and the limit of detection (LOD) were  $1.0 \times 10^{-10}$  -  $2.0 \times 10^{-8}$  M and  $2.0 \times 10^{-11}$  M (S/N = 3), respectively.

Keywords: 3-PNO, Modification, Cu(II) ion analysis

## Özet

Bakır (Cu (II)) çok düşük seviyelerde birçok bitki ve hayvan için gerekli ve gerekli bir mikro besleyicidir. Bununla birlikte, hücre zarları ile birleşmesi nedeniyle su bitkileri için yüksek seviyelerde toksiktir. Camı karbon elektrot (GCE), 3-fenil-4-[2-(2-naftilsülfoniloksi)-benzilamino]-4,5-dihidro-1H-1,2,4-triazol-5-on (3-PNO) ile 0,1 M destek elektrot içinde modifiye edildi. Modifiye edilmiş yüzey dönüşümlü voltametri (CV) ve X-ışınları fotoelektron spektroskopisi ile karakterize edildi. Karakterizasyon sonuçlarına göre modifiye elektrot başarılı bir şekilde elde edildi. 3-PNO ile modifiye edilmiş GCE, Cu(II) iyonunun su numunesinin içinde analizi için kullanıldı. Konsantrasyon aralığı ve deteksiyon limiti sırasıyla  $1.0 \times 10^{-10}$  -  $2.0 \times 10^{-8}$  M ve  $2.0 \times 10^{-11}$  M (S/N = 3), olarak bulundu.

Anahtar kelimeler: 3-PNO, Modifikasyon, Cu(II) iyon analizi

## 1 Introduction

Because of various applications in industrial and agricultural processes, Cu(II) can be released into the environment from many sources. Drinking water can be a potential source for an intense Cu(II) exposition because of the production and industrial use [1, 2]. Copper(II) is highly toxic for drinking water, and mercury is the only metal more toxic than copper [4]. The chemically modified electrodes in electrochemistry have been interesting research area in recent years [5]. Surfaces with modifier and sensors are crucial topic in nanotechnology development. These surfaces are used for crucial targets such as metal detection, sensor development and drug analysis [6]. The one of the most important methods is phenol oxidation to create modified electrodes such as carbon [9]. The modified electrodes are investigated by electrochemistry and XPS [10, 11]. Important papers about Cu(II) ion detection were reported using spectrophotometric methods [12]. However, the techniques have difficult methods to eliminate the excipients. The electrochemical methods can eliminate these difficulties. Because of their speed and sensitivity, the sensitive electrochemical signals can be obtained [13]. In this report, we firstly formed GCE modified with 3PNO (3PNO/GCE). 3PNO was utilized as the modifier because it was grafted onto the carbon area by phenol oxidation. The 3PNO/GCE was characterized by CV and XPS. In addition, the 3PNO/GCE was used for Cu(II) ions analysis with high selectivity and sensitivity.

## 2 Experimental Section

### 2.1 Reagents

All used chemicals are reagent grade quality. The water samples were taken from Pamukkale University. The 3-PNO/GCE was utilized for working electrode. The acetic acid/sodium acetate was used as supporting electrolyte. The amount of Cu(II) was obtained by calibration technique.

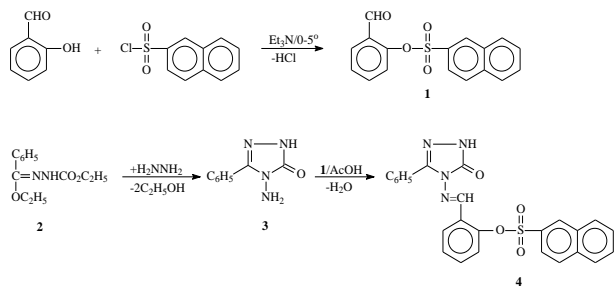
### 2.2 Instrumentation

The whole experiments were done by IviumStat (U.S) with C3 Cell stand [14]. The modification of GCE was performed in 0.1M 3PNO in 0.1M supporting electrolyte between +0.0 V and +3.0 V. Melting point and IR spectra were obtained according to our previous paper [15]. Elemental analysis of the new compound was made in CHNS elemental analyzer.

### 2.3 3-PNO (compound 4) synthesis

3-Phenyl-4-amino-4,5-dihydro-1H-1,2,4-triazol-5-one (3) (0.76 g, 0.01 mol) was dissolved in acetic acid (20 mL) and treated with 2-naphthylsulfonyloxybenzaldehyde) 1 (3.12 g, 0.01 mol). The recrystallizations in ethanol formed 3. Yield: 4.57 g (97 %); mp: 213 °C; IR (KBr) 1697 (C=O), 1589 (C=N), 1346 and 1182 (SO<sub>2</sub>), 763 (1,2-disubstituted benzenoid ring), 763 and 692 (monosubstituted benzenoid ring); <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): 7.39 (Ar-H, J = 8.40 Hz), 7.49 (m, Ar-H), 7.57-7.65 (m, 5H, Ar-H), 7.71 (d, 1H, Ar-H, J = 8.00 Hz), 8.13 (d, 1H, Ar-H, J = 8.40 Hz), 8.61 (s, 1H, Ar-H), 9.72 (s, 1H, N=CH), 12.37 (s, 1H, NH); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): 122.47, 123.74

127.00, 127.71 (arom C), 127.95 (C), 128.02, 128.23 (arom C), 128.28 (2C), 129.36, 129.80, 129.98, 130.13, 130.31, 130.34, 132.89, 135.12, 144.26 (arom C), 147.55 (triazole C3), 148.04 (N=CH), 151.08 (triazole C2), 151.15 (triazole C4), 151.20 (triazole C5), 151.22 (triazole C6), 151.24 (triazole C7), 151.26 (triazole C8), 151.28 (triazole C9), 151.30 (triazole C10), 151.32 (triazole C11), 151.34 (triazole C12), 151.36 (triazole C13), 151.38 (triazole C14), 151.40 (triazole C15), 151.42 (triazole C16), 151.44 (triazole C17), 151.46 (triazole C18), 151.48 (triazole C19), 151.50 (triazole C20), 151.52 (triazole C21), 151.54 (triazole C22), 151.56 (triazole C23), 151.58 (triazole C24), 151.60 (triazole C25), 151.62 (triazole C26), 151.64 (triazole C27), 151.66 (triazole C28), 151.68 (triazole C29), 151.70 (triazole C30), 151.72 (triazole C31), 151.74 (triazole C32), 151.76 (triazole C33), 151.78 (triazole C34), 151.80 (triazole C35), 151.82 (triazole C36), 151.84 (triazole C37), 151.86 (triazole C38), 151.88 (triazole C39), 151.90 (triazole C40), 151.92 (triazole C41), 151.94 (triazole C42), 151.96 (triazole C43), 151.98 (triazole C44), 152.00 (triazole C45), 152.02 (triazole C46), 152.04 (triazole C47), 152.06 (triazole C48), 152.08 (triazole C49), 152.10 (triazole C50).  
(470.50): C, 63.82; H, 3.86; N, 11.91; S, 6.81. Found: C, 62.84; H, 3.89; N, 11.87; S, 6.77 (Scheme 1).

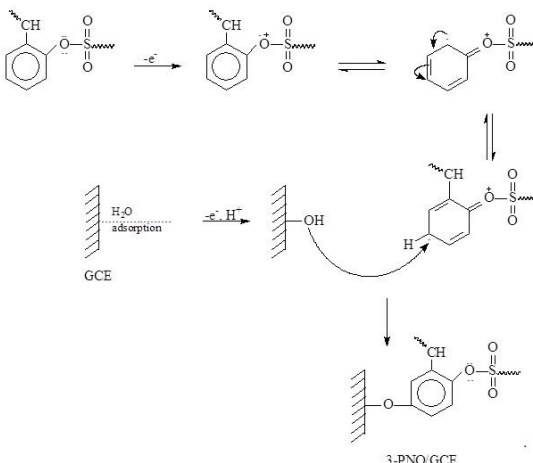


Scheme 1. Synthesis route of PNO.

### 3 Results and Discussion

#### 3.1 GCE modification

When the scanning potential is reached to the oxygen oxidation, the glassy carbon electrode is oxidized. This situation causes the alcoholic species. These form the residual water in the range of 10 to 10<sup>6</sup> M. Hence, etheric bond (GOOC(3-PNO)) was on the modified surface (Scheme 2) [16].



Scheme 2. The PNO linkage to GCE.

The voltammograms of redox probes are shown in Fig. 1. The clear peaks of redox probes at the bare GCE are not seen by 3 PNO/GCE. These suppressive peaks are indicative to the formation of 3-PNO modified surfaces. The development of 3-PNO/GCE was presented by XPS. The certain bands verified the presence of 3-PNO/GCE (Fig. 2). The situation indicated the formation of 3-PNO/GCE.

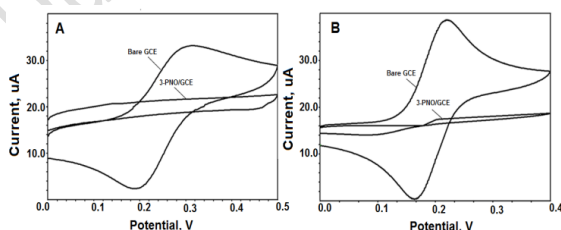


Figure 1. Cyclic voltammograms of (A) 1.0 mM potassium ferricyanide, (B) 1.0 mM ferrocene.

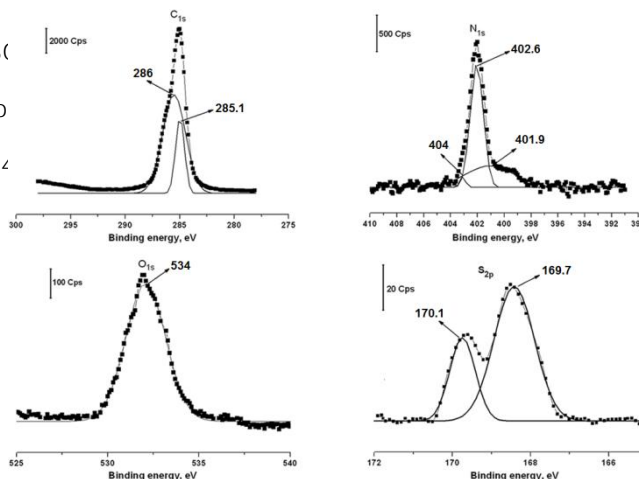


Figure 2. XPS spectrum of PNO/GCE surface.

#### 3.2 Optimization of analytical conditions

When we obtain the most optimal pH, we tried different pH in acetate buffer of pH 5.5 (Fig. 3A). So, the most suitable is 5.5 pH. After that, the PNO/GCE was treated with different periods (5, 10, 15, 20, 25 min). According to Fig. 3B, it reached to maximum value at 15 min (Fig. 3B).

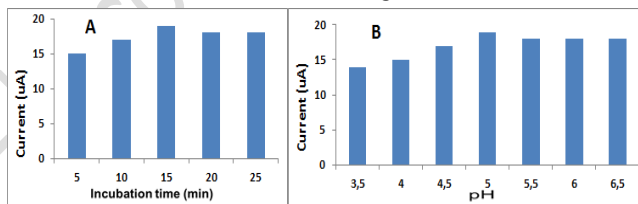


Figure 3. Voltammetric responses of PNO / GCE for 2.0 x 10<sup>-5</sup> M of Cu(II) at (A) time and (B) pH (n=6).

#### 3.3 Analytical application

The voltammograms of Cu(II) ion on PNO/GCE are shown in Fig. 4. The peak values of Cu(II) ion are linear with 20.0 nM. The regression equation of Cu(II) is 0.0519. The limit of quantitation and LOD for Cu(II) was 5.19 nM. The PNO/GCE was applied to water sample. 5.19 nM Cu(II) amount was determined by atomic absorption spectrometry. The results by two methods are in well agreement.

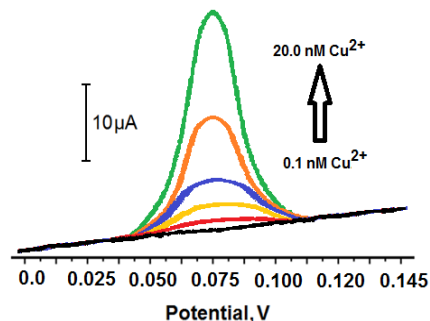


Figure 4. The voltammograms with Cu(II) concentrations.

### 4 Conclusion

An electrode is developed by modification of PNO on the GCE. The modification formations were characterized by CV and XPS. LOQ and LOD for Cu(II) were 5.19 nM and 1.0 nM, respectively.

developed electrode suggests good sensitivity analysis of target.

#### 4 Acknowledgment

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