

A novel Cu(II) detection assay via modified glassy carbon electrode Modifiye edilmiş camı 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 1.0×10^{-10} - 2.0×10^{-8} M and 2.0×10^{-11} M ($S/N = 3$), respectively.

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

Öz

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 1.0×10^{-10} - 2.0×10^{-8} M ve 2.0×10^{-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 [3],[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]-[8]. 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 3-PNO (3-PNO/GCE). 3-PNO was utilized as the modifier because it was grafted onto the carbon area by phenol oxidation. The 3-PNO/GCE was characterized by CV and XPS. In addition, the 3-PNO/GCE was used for of 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 0.1 M acetic acid/sodium acetate was used as supporting electrolyte. The amount of Cu(II) was obtained by calibration technique.

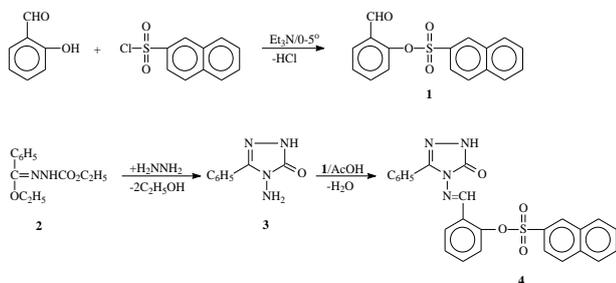
2.2 Instrumentation

The whole experiments were done by IviumStat (U.S) with C3 cell stand [14]. The modification of GCE was performed in 1.0 mM 3-PNO 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-932 elemental analyzer.

2.3 3-PNO (compound 4) synthesis

3-Phenyl-4-amino-4,5-dihydro-1H-1,2,4-triazol-5-one (3) (1.76g, 0.01 mol) was dissolved in acetic acid (20 mL) and treated with 2-(2-naphthylsulfonyloxy)benzaldehyde 1 (3.12 g, 0.01 mol). The recrystallizations in ethanol formed 3-PNO. Yield: 4.57 g (97%); mp: 213 °C; IR (KBr, v, cm⁻¹): 3190 (NH), 1697 (C=O), 1589 (C=N), 1346 and 1182 (SO₂), 763 (1,2-disubstituted benzenoid ring), 763 and 692 (monosubstituted benzenoid ring); ¹H NMR (400 MHz, DMSO-d₆): δ 7.39 (d, 1H, Ar-H, J = 8.40 Hz), 7.44-7.49 (m, 4H, 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); ¹³C NMR (100 MHz, DMSO-d₆): δ 122.47, 123.74, 126.11, 126.31, 127.00, 127.71 (arom-C), 127.95 (2C), 128.02, 128.23 (arom-C), 128.28 (2C), 129.36, 129.80, 129.98, 130.13, 130.31, 130.74, 131.34, 132.89, 135.12, 144.26 (arom-C), 147.55 (triazole C3), 148.04 (N=CH), 151.08 (triazole C5); UV λ_{max} (λ): 260 (21.343), 238 (27.906) nm; Anal. Calcd. for C₂₅H₁₈N₄O₄S (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).

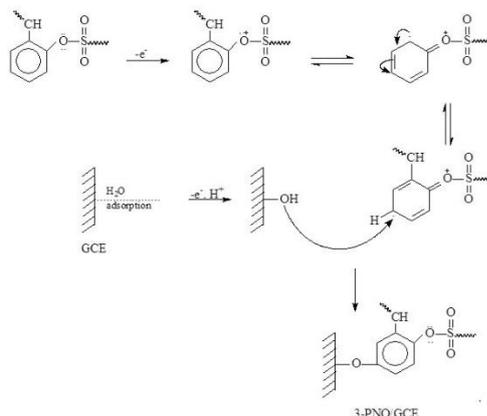


Scheme 1: Synthesis route of 3-PNO.

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^{-3} to 10^{-2} M. Hence, etheric bond (GC)C-O-C(3-PNO) was on the modified surface (Scheme 2) [16].



Scheme 2: The 3-PNO linkage to GCE.

The voltammograms of redox probes are shown in Figure 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 (Figure 2). The situation indicated the formation of 3-PNO/GCE.

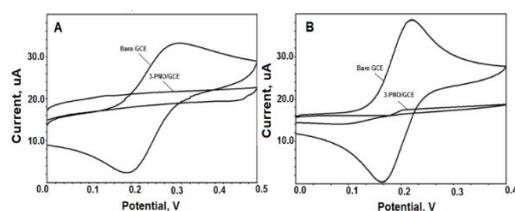


Figure 1: Cyclic voltammograms of (A) 1.0 mM potassium ferricyanide, (B) 1.0 mM ferrocene.

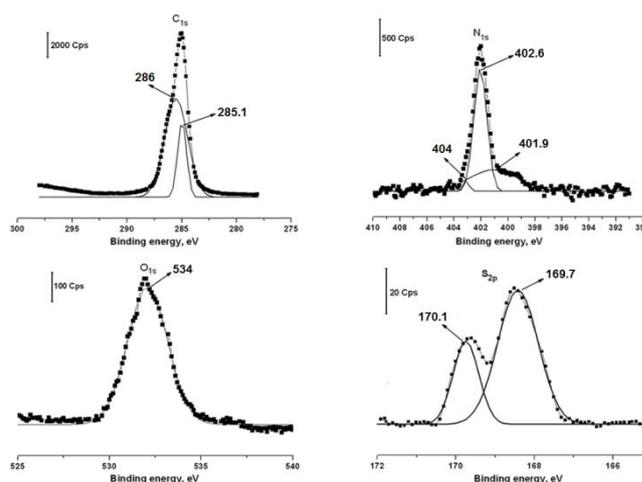


Figure 2: XPS spectrum of 3-PNO/GCE surface.

3.2 Optimization of analytical conditions

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

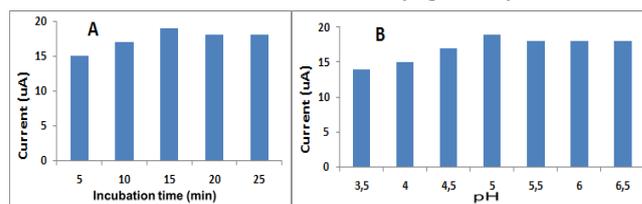


Figure 3: Voltammetric responses of 3-PNO/GCE for 2.0×10^{-8} M of Cu(II) at (A) time and (B) pH (n=6).

3.3 Analytical application

The voltammograms of Cu(II) ion on 3-PNO/GCE are shown in Figure 4. The peak values of Cu(II) ion are linear with 0.1-20.0 nM. The regression equation of Cu(II) is y (uA) = $0.9564x$ (nM) + 0.0519. The limit of quantitation (LOQ) for Cu(II) was 1.0×10^{-10} M and LOD for Cu(II) was 2.0×10^{-11} M. The 3-PNO/GCE was applied to water samples. Cu(II) amount was 1.64×10^{-9} M Cu(II) amount was 1.66×10^{-9} M by atomic absorption spectrometry. The results by two methods are in well agreement.

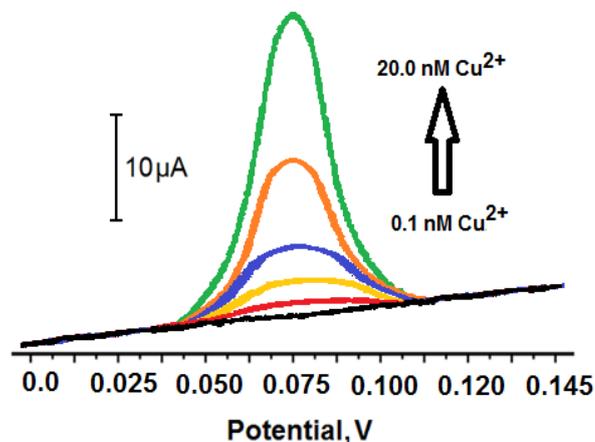


Figure 4: The voltammograms with Cu(II) concentrations.

4 Conclusion

A electrode is developed by modification of 3-PNO. The modification formations were characterized by CV and XPS. LOQ and LOD for Cu(II) were 1.0×10^{-10} and 2.0×10^{-11} M. The developed electrode suggests good sensitivity in the analysis of target.

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6 References

- [1] Parmar P, Daya S. "The effect of copper on (3H)-tryptophan metabolism in organ cultures of rat pineal glands". *Metabolic Brain Disease*, 16, 199-205, 2001.
- [2] Zhou Y, Wang S, Zhang K, Jiang X. "Visual detection of copper(II) by azide-and alkyne-functionalized gold nanoparticles using click chemistry". *Angewandte Chemie International Edition*, 47, 7454-7456, 2008.
- [3] Liu C, Bai R, Ly QS. "Selective removal of copper and lead ions by diethylenetriamine-functionalized adsorbent: Behaviors and mechanisms". *Water Research*, 42, 1511-1522, 2008.
- [4] Peric J, Trgo M, Medvidovic NV. "Removal of zinc, copper and lead by natural zeolite-a comparison of adsorption isotherms". *Water Research*, 38, 1893-1899, 2004.
- [5] Gupta VK, Yola ML, Atar N, Solak AO, Uzun L, Üstündağ Z. "Electrochemically modified sulfisoxazole nanofilm on glassy carbon for determination of cadmium(II) in water samples". *Electrochimica Acta*, 105, 149-156, 2013.
- [6] Oztekin Y, Tok M, Nalvuran H, Kiyak S, Gover T, Yazicigil Z, Ramanaviciene A, Ramanavicius A. "Electrochemical modification of glassy carbon electrode by poly-4-nitroaniline and its application for determination of copper(II)". *Electrochimica Acta*, 56, 387-395, 2010.
- [7] Oztekin Y, Krikstolaityte V, Ramanaviciene A, Yazicigil Z, Ramanavicius A. "1,10-Phenanthroline derivatives as mediators for glucose oxidase". *Biosensors and Bioelectronics*, 26, 267-270, 2010.
- [8] Yola ML, Atar N. "A novel voltammetric sensor based on gold nanoparticles involved in p-aminothiophenol functionalized multi-walled carbon nanotubes: Application to the simultaneous determination of quercetin and rutin". *Electrochimica Acta*, 119, 24-31, 2014.
- [9] Downard AJ, Tan ESQ, Yu SSC. "Controlled assembly of gold nanoparticles on carbon surfaces". *New Journal of Chemistry*, 30(9), 1283-1288, 2006.
- [10] Tsierkezos NG, Ritter U. "Application of electrochemical impedance spectroscopy for characterisation of the reduction of benzophenone in acetonitrile solutions". *Physics and Chemistry of Liquids*, 49(6), 729-742, 2011.
- [11] Yola ML, Eren T, Atar N. "A novel and sensitive electrochemical DNA biosensor based on Fe@Au nanoparticles decorated graphene oxide". *Electrochimica Acta*, 125, 38-47, 2014.
- [12] Bortoleto GG, Macarovsca GT, Cadore S. "Determination of cadmium by flame-atomic absorption spectrometry after preconcentration on silica gel modified with cupferron". *Journal of the Brazilian Chemical Society*, 15, 313-317, 2004.
- [13] Liu M, Feng Y, Wang G, Fang B. "Determination of cadmium(II) using glassy carbon electrodes modified with cupferron, β -naphthol, and multiwalled carbon nanotubes". *Microchimica Acta*, 177(1), 221-228, 2012.
- [14] Yola ML, Atar N, Qureshi MS, Üstündağ Z, Solak AO. "Electrochemically grafted etodolac film on glassy carbon for Pb(II) determination". *Sensors and Actuators B: Chemical*, 171-172, 1207-1215, 2012.
- [15] Yüksek H, Koca E, Gürsoy-Kol Ö, Akyıldırım O, Çelebier M. "Synthesis, in vitro antioxidant activity, and physicochemical properties of novel 4,5-dihydro-1H-1,2,4-triazol-5-one derivatives". *Journal of Molecular Liquids*, 206, 359-366, 2015.
- [16] He JB, Jin GP, Chen QZ, Wang Y. "A quercetin-modified biosensor for amperometric determination of uric acid in the presence of ascorbic acid". *Analytica Chimica Acta*, 585(2), 337-343, 2007.