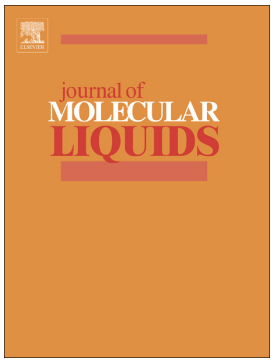

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Electrochemical Detection of Atrazine in Wastewater Samples by Copper Oxide (CuO) Nanoparticles Ionic Liquid Modified Electrode

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ABSTRACT

In the present report, a new voltammetric sensor based on copper oxide nanoparticles involved in 2-(3-acetoxy-4-methoxybenzylidenamino)-thiophenol (AMT) ionic liquid (CuO NPs/ILs) was developed for atrazine (ATR) analysis. Firstly, the CuO NPs/ILs modified surface was investigated by using transmission electron microscopy (TEM), x-ray diffraction (XRD), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and energy dispersive x-ray analysis (EDX). The linearity range and the detection limit (LOD) of the prepared sensor were calculated as 1.0×10^{-11} – 2.0×10^{-9} and 2.0×10^{-12} M, respectively. Voltammetric sensor was also applied to wastewater samples with high recovery.

Keywords: Atrazine; CuO nanoparticles; Ionic liquid; Square wave voltammetry

1. Introduction

The insects and some pests can be controlled by using the carcinogenic and cytotoxic drugs. Nonetheless, many debris can come into the life chain such as water and food. Due to these factors, the significant health and ecosystem problems emerge worldwide [1, 2]. ATR, 1-chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine, has triazine groups. It is one of the most common pesticides [3, 4]. However, ATR as drug can be unconsciously used by farmers. This situation causes the contamination of many water sources. Hence, the environment and food chain adversely are affected [5]. Because of these reasons, early analysis of ATR is needed in natural samples in terms of ecosystem and people. In the literature, the methods such as gas chromatography–mass spectrometry [6], thin-layer chromatography, high-performance liquid chromatography [7] and gas micellar electro kinetic chromatography [8] were presented for this analysis. Nevertheless, when we want to investigate these methods in terms of material consumption and expensiveness, there are many negative situations. Due to these reasons, more sensitive, low-cost, simple and selective sensors based on nanoparticles and nanomaterials are needed [9-12]. There are several reports dealing with determination of ATR. The quartz crystal microbalance (QCM) technique was developed based on ATR imprinted polymer [13]. However, the film decompositions on gold chip frequently occur in comparison with carbon paste electrode. In addition, the expensive electrodes such as gold were used for determination of ATR [14].

Ionic liquids have high conductivity. Because of this situation, they are promising mediator in sensor applications [15, 16]. In addition, owing to high ionic conductivity, fast ion mobility and ionic liquids can be used as electrolyte in the development of voltammetric sensor [17-19].

The electrochemical detection of ATR has been not performed by CuO NPs/ILs up to now. The novel electrochemical method based on CuO NPs/ILs was developed for selective

and sensitive analysis. Firstly, CuO NPs/ILs nanomaterial was prepared. After that, CuO NPs/ILs modified electrodes were developed. Finally, the electrodes were applied to wastewater samples for ATR analysis.

2. Experimental

2.1. Materials

ATR was obtained from Sigma–Aldrich. The stock solutions of ATR (1.0 mM) were prepared with 0.1 M phosphate buffer solution (PBS) (pH 7.0). Copper sulfate heptahydrate [$CuSO_4.7H_2O$], acetonitrile (MeCN), ethanol (EtOH), isopropyl alcohol (IPA), sodium hydroxide (NaOH), liquid paraffin and graphite powder were purchased from Sigma–Aldrich (USA).

2.2. Instrumentation

Electrochemical experiments were employed by IviumStat (U.S) equipped with C3 cell stand. JEOL 2100 HRTEM (JEOL Ltd., Tokyo, Japan) was utilized for the characterization of nanocomposites. A Rigaku Miniflex X-ray diffractometer (Japan) using monochromatic CuKα radiation was utilized for XRD.

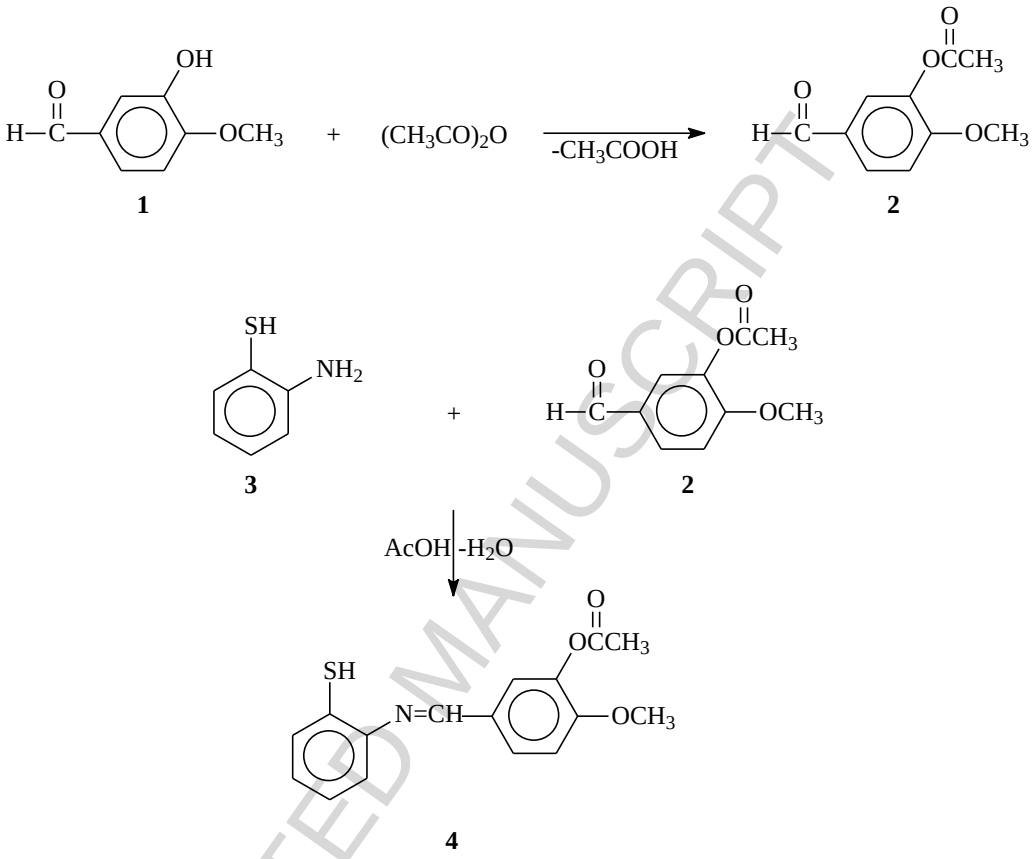
2.3. Synthesis of CuO nanoparticles

0.5 M $CuSO_4.7H_2O$ and 0.5 M NaOH were prepared in distilled water. The 0.5 M NaOH solution put into the beaker. After that, it was heated to 60 ^oC. The 0.5 M $CuSO_4.7H_2O$ solution was slowly added into the hot NaOH solution. After the precipitation, the mixture was washed with distilled water and dried at 100 ^oC for 10 h.

2.4. Synthesis of AMT

3-Hydroxy-4-methoxybenzaldehyde 1 (0.01 mol) was refluxed with acetic anhydride (20 mL) for 0.5 h. After pure EtOH (100 mL), the mixture was refluxed for 0.5 h. After evaporation of the resulting solution at 40-45 °C, several recrystallizations of the residue from EtOH gave pure compound 2 (3-acetoxy-4-methoxybenzaldehyde) [20]. 2-aminothiophenol

(0.01 mol) was dissolved in acetic acid (20 mL) and treated with compound 2 (0.01 mol). The mixture was refluxed for 2 h and then evaporated at 50-55 °C. After recrystallization, the compound 4 (AMT) was obtained.



Scheme 1. Synthesis route of compound 4 (AMT)

2.5. Electrode preparation

The used electrode in this study such as CuO NPs/ILs modified carbon paste electrode (CuO NPs/ILs/CPE) was developed according to the report [16].

2.6. Sample preparation

The sample was prepared according to our previous protocol [21].

3. Results and discussion

3.1. Characterization of nanostructures

The presence of CuO NPs on a lighter structure is seen clearly (Fig. 1A). The average diameters of spherical CuO NPs as dark dots are 15-20 nm. Thus, this situation indicated that CuO NPs was successfully prepared. In addition, the analysis of EDX confirms the formation of CuO NPs. The Cu and O elements were observed in Fig. 1B.

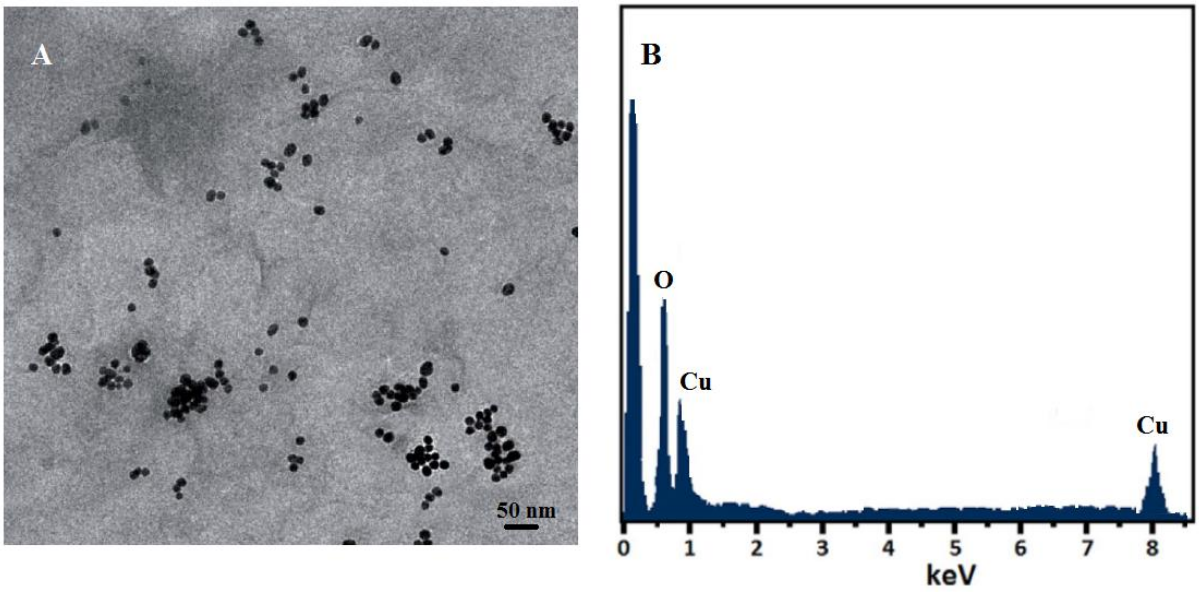


Figure 1. (A) TEM image of CuO NPs and (B) EDX image of CuO NPs

Fig. 2 shows the XRD spectra of CuO NPs. the peaks indicated to the monoclinic crystal system CuO NPs. The sharp structural peaks and crystallite size less than 50 nm shows the nanocrystalline nature of CuO NPs.

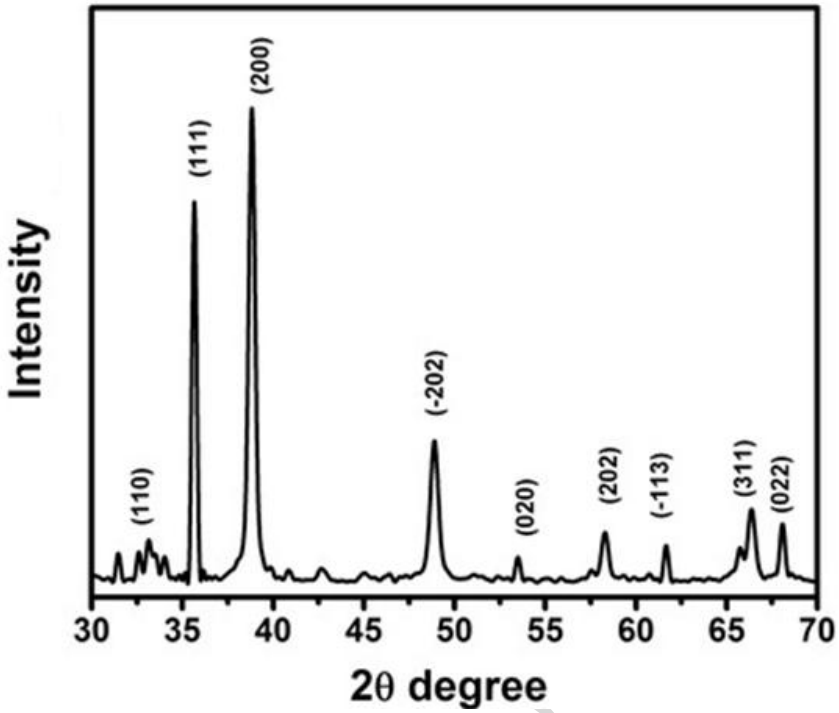


Figure 2. XRD spectra of CuO NPs

3.2. Electrochemical studies

1.0 mM $[Fe(CN)_6]^{3-}$ was used for the characterizations of developed electrodes such as bare CPE, CuO NPs/CPE, ILs/CPE and CuO NPs/ILs/CPE. The obvious reversible peaks of 1.0 mM $[Fe(CN)_6]^{3-/4-}$ with 200 mV of peak potential difference (ΔEp) is seen at bare CPE (curve a of Fig. 3A). After modification of CuO NPs on bare CPE, ΔEp decreased to 130 mV with a small increase in the peak current (curve b of Fig. 3A). The more catalytic increase was shown when ILs/CPE was used as working electrode (ΔEp = 80 mV on curve c of Fig. 3A). Finally, when CuO NPs/ILs/CPE was used for working electrode, the more catalytic ability and the less peak potential difference were obtained against redox probe (ΔEp = 40 mV on curve d of Fig. 3A). The obtained results were confirmed by using EIS experiments. Fig. 3B shows the impedance plot of (a) bare CPE (curve a), (b) CuO NPs/CPE (curve b), (c) ILs/CPE (curve c) and (d) CuO NPs/ILs/CPE (curve d) surfaces. The obtained charge transfer resistance (R_{ct}) values of the prepared electrodes are 135.0 ohm, 98.0 ohm, 73.0 and 48.0

ohm, respectively. According to Fig. 3A and Fig. 3B, R_{ct} values are consistent with CV results.

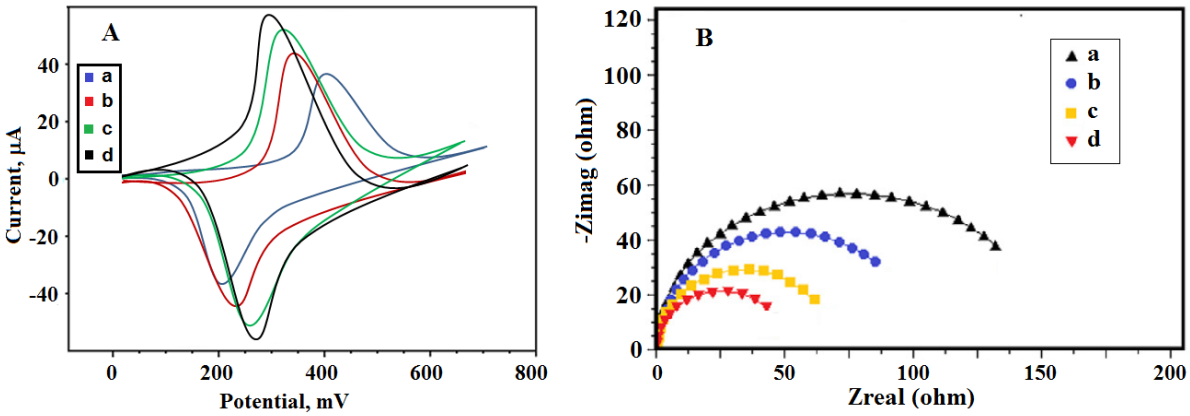


Figure 3. (A) Cyclic voltammograms at (a) bare CPE, (b) CuO NPs/CPE, (c) ILs/CPE, (d) CuO NPs/ILs/CPE; (B) EIS response at (a) bare CPE, (b) CuO NPs/CPE, (c) ILs/CPE, (d) CuO NPs/ILs/CPE. Redox probe: 1.0 mM $[Fe(CN)_6]^{3-}$ solution containing 0.1 M KCl, Scan rate: 100 mV s^{-1}

3.3. pH effect

The pH effect on ATR response was investigated in range of 3.0-9.0. The low and high pH conditions caused the low current signal of ATR on modified electrode. The protonation of ATR at the low pH and the ionic form of ATR at the high pH affected negatively the extraction efficiency [21]. Thus, we selected 7.0 as optimum pH.

3.4. Linearity range of proposed sensor

The square wave voltammograms (SWVs) of various concentrations of template molecule (Fig. 4) indicate that the current increases linearly with ATR concentration. The five measurements were performed for calibration graph. The regression equation (inset of Fig. 4) is y (µA) = 5.6061x (nM) + 0.2121. Limit of quantification (LOQ) and LOD were obtained as 1.0×10^{-11} M and 2.0×10^{-12} M, respectively.

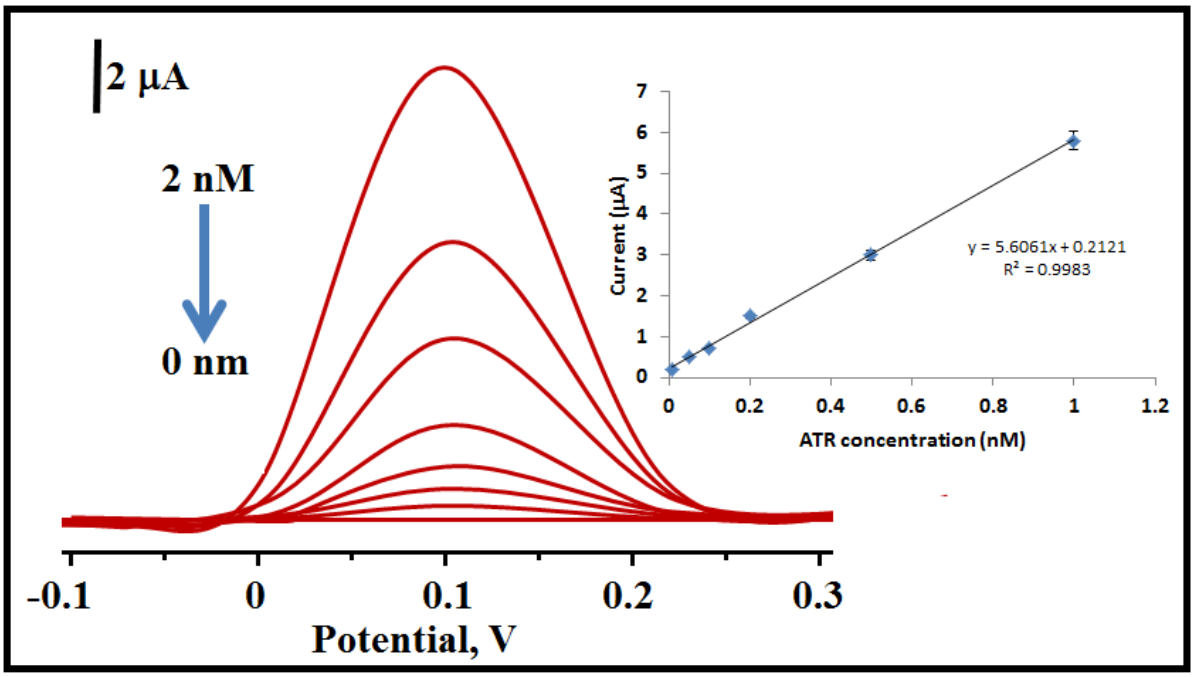


Figure 4. SWVs of the CuO NPs/ILs/CPE (from blank solution without ATR to 2.0 nM ATR in pH 7.0 of PBS) Inset: The calibration curves of ATR

3.5. Recovery and Selectivity

The recovery was examined in wastewater samples (Table 1). As seen in the obtained values, they are very close to 100.00%. According to the results, we can say that the CuO NPs/ILs/CPE sensor in this report has high selectivity. In addition, to verify the high selectivity, the standard addition technique was applied to the wastewater samples. The obtained equation is y (µA) = 5.6098x (nM) + 7.937. Hence, the effect of interference from wastewater sample was not importantly seen.

Table 1. Recovery of ATR in wastewater samples (n=6)

Sample	Added ATR (nM)	Found ATR (nM)	Recovery (%)
Wastewater	-	1.73±(0.04)	-
	0.10	1.84(± 0.01)	100.55 ± 0.7
	0.20	1.91(± 0.02)	98.96 ± 0.3
	0.30	2.04(± 0.08)	100.49 ± 1.3

3.6. Reproducibility and stability of the CuO NPs/ILs/CPE

The six different electrodes were prepared with same procedure. For the obtained current signals, the value of relative standard deviation is 0.37%. This situation shows the fabrication reliability.

The stability of one electrode (CuO NPs/ILs/CPE) was examined. During 30 days, the signal was frequently measured. The mean value is 99.17% of the first signal. The mean value indicates that CuO NPs/ILs/CPE is utilized in long-term.

4. Conclusions

In this report, a new electrochemical sensor was developed and applied for the determination of atrazine in wastewater samples. According to the obtained data, the prepared CuO NPs/ILs/CPE was well characterized by using TEM, EDX, EIS, CV and XRD. The sensor shows high selectivity and sensitivity towards atrazine detection in wastewater matrix. Because of these reasons, we can say that the electrochemical sensor was utilized for the routine analysis without interference.

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Research Highlights

> We developed a new electrochemical sensor for determination of atrazine

> CuO nanoparticles ionic liquid nanocomposite was characterized

> The voltammetric sensor was applied to wastewater samples

> The developed nanosensor sensor might be preferred to the other analytical methods