



Original scientific paper

## Electrochemical sensor for acetylcholine detection based on WO<sub>3</sub> nanorods-modified glassy carbon electrode

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### Abstract

Acetylcholine (ACH) is one of the excitatory neurotransmitter in the human body. It is the most abundant neurotransmitter responsible for triggering the activation of postsynaptic neurons, leading to an excitatory response. ACH plays a crucial role in various physiological processes, including muscle contraction, autonomic nervous system regulation, and cognitive functions such as learning and memory. In this study, an electrochemical sensor was prepared based on WO<sub>3</sub> nanorods modified glassy carbon electrode for the detection of ACH. The WO<sub>3</sub> nanorods provided excellent properties for the electrochemical determination of ACH. The proposed sensor exhibited a wide linear detection range of (0.1 to 400.0 μM) and a low detection limit of 0.025 μM for ACH. These results demonstrate the sensor's high sensitivity in detecting this important neurotransmitter. In addition the developed sensor showed good ability for ACH determination in real samples. This study offers an innovative strategy for the electrochemical detection of ACH, showcasing the potential of nanomaterials in the development of advanced sensing technologies.

### Keywords

Cyclic voltammetry; differential pulse voltammetry, modified electrodes, real sample analysis, neurotransmitter

### Introduction

Acetylcholine (ACH) is a prominent neurotransmitter found throughout the central and peripheral nervous systems. ACH is vital for various cognitive processes in the human CNS, including memory, learning, attention, sleep, and consciousness. Dysfunction of the cholinergic system has

been clinically linked to certain neuropsychiatric disorders, like Alzheimer's, and Parkinson's diseases. However, the precise effects of ACH in the brain on cognitive functions and neuropsychiatric disorders remain not fully understood. As a result, there is a pressing need to develop rapid and sensitive *in vivo* techniques for measuring ACH [1-3]. To this end, researchers have developed a variety of analytical techniques that enable the reliable and quantitative determination of ACH concentrations in various biological samples, such as LC-MS/MS, fluorescence spectroscopy, high-performance liquid chromatography (HPLC) and colorimetry [4-7]. However, these measurement methods are frequently time-consuming, costly, and necessitate extensive sample preparation before analysis. Electrochemical techniques offer significant advantages for the real-time quantitative analysis of analytes, as they are generally faster, more user-friendly, and can provide continuous and reversible responses without interference from the sample [8-15]. Electrochemical sensors typically consist of a transducer coated with a chemical or biological recognition layer, where the interaction between the target analyte and the sensitive layer provides the analytical information [16-25].

In recent years, the rapid progress of nanoscience has resulted in the emergence of nano-materials with distinctive photonic, catalytic, electronic, and magnetic properties owing to their high surface area, specific morphologies, and various applications [26-35]. Especially, the high surface-to-volume ratio, high chemical stability, prominent electrical conductivity, and biocompatibility of nanostructures can significantly increase their use in electrochemical sensors and biosensors [36-46]. Among various nanomaterials, nanostructured tungsten oxides (WO<sub>3</sub>) have attracted considerable attention due to their large surface area and other good properties. WO<sub>3</sub> nanostructures have been widely applied in numerous fields, such as gas sensing, photocatalysis, *etc.* [47-50].

In this study, we developed a sensitive and convenient non-enzymatic electrochemical sensor for ACH detection. The non-enzymatic electrochemical sensors are very advantageous due to their low cost, stability, and easy preparation. The sensor was made by attaching WO<sub>3</sub> nanorods (NRs) to the surface of the glassy carbon electrode (GCE). The electrocatalytic properties of the sensor WO<sub>3</sub>-NRs-modified GCE were investigated using cyclic voltammetry (CV), chronoamperometry and differential pulse voltammetry (DPV). WO<sub>3</sub> NR/GCE sensor provides a new method for sensitive detection of ACH.

## Experimental

### *Instruments and chemicals*

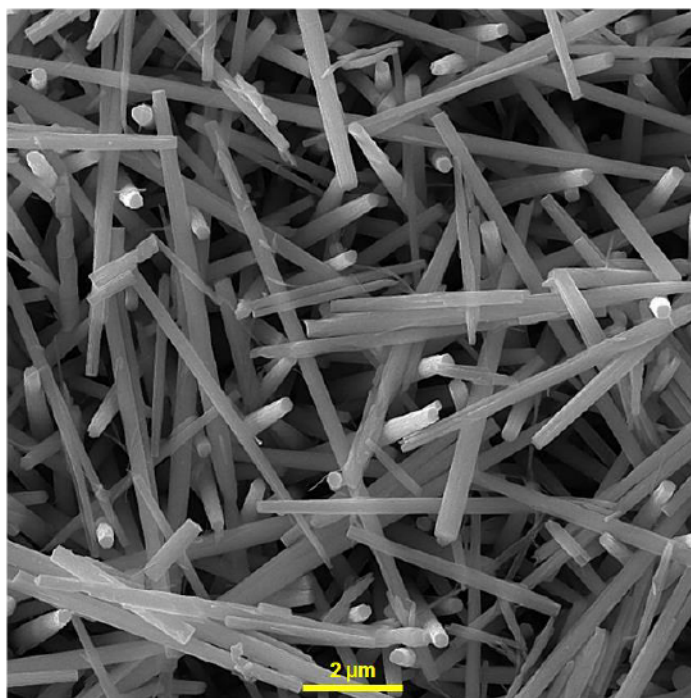
The electrochemical measurements were conducted using an Autolab PGSTAT 302N system (Eco Chemie, the Netherlands). A Metrohm pH meter (model 710) was used to measure the pH of the solutions. The chemicals, ACH, NaOH, H<sub>3</sub>PO<sub>4</sub> and other chemicals used in the study were of analytical grade and were used as received, without any additional purification. These chemicals were purchased from Merck and Sigma-Aldrich companies.

The synthesis and characterization of WO<sub>3</sub> NRs were described in our previous work [51]. Figure 1 shows the FE-SEM image of WO<sub>3</sub> NRs.

### *Modification of GCE modified with WO<sub>3</sub> nanorods*

The bare GCE was carefully pretreated by polishing with an alumina slurry on a polishing cloth. After polishing, the electrode was washed with double-distilled water. Next, 1.0 mg of WO<sub>3</sub> NR was added to 1 mL of double-distilled water. The suspension was then sonicated for approximately 30 minutes to ensure homogeneous dispersion of the nanorods. Lastly, the solvent was allowed to evaporate at room temperature, immobilizing the WO<sub>3</sub> NRs immobilized on the GCE surface. This

immobilization of the synthesized nanomaterial onto the GCE surface was a crucial step in the fabrication of the electrochemical sensor device.

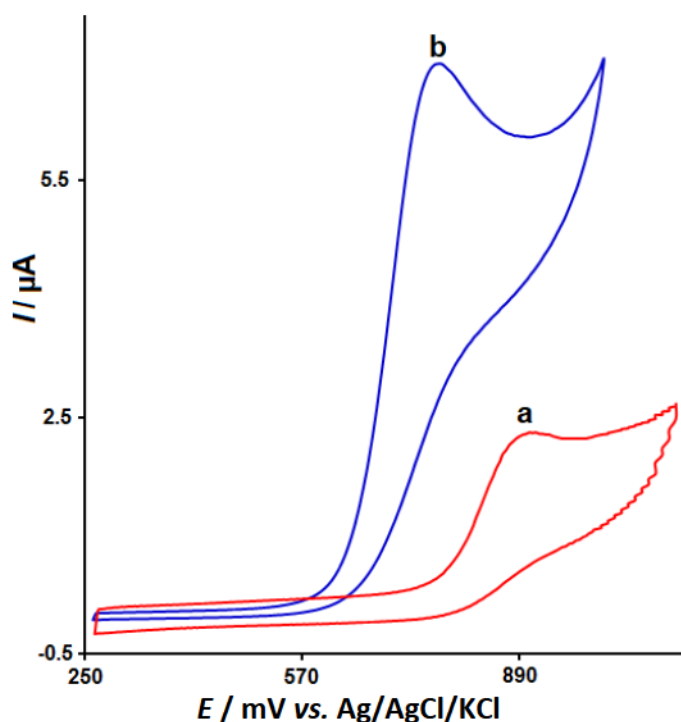


*Figure 1. FE-SEM image of WO<sub>3</sub> NRs*

## Results and discussion

### *Electrochemical activity of ACH on WO<sub>3</sub> NRs/GCE*

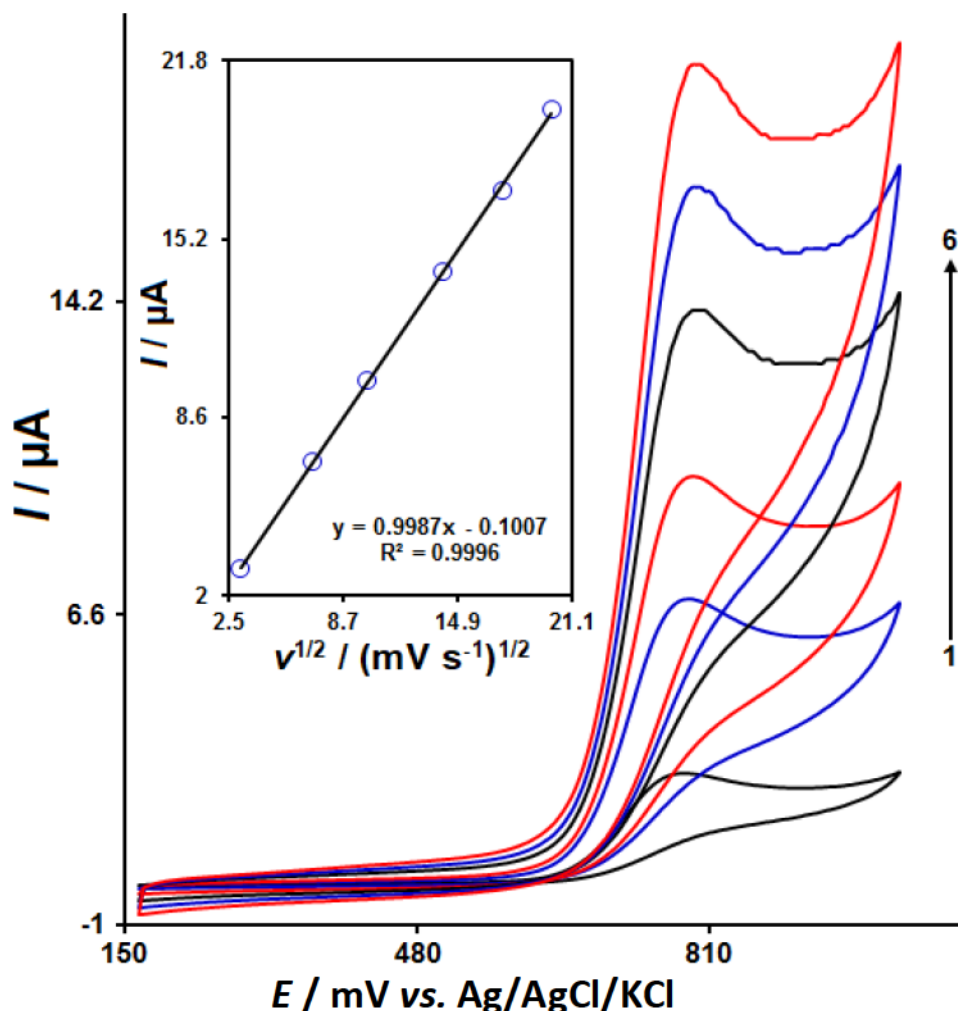
The electrochemical characteristics of the WO<sub>3</sub> NRc/GCE were investigated using cyclic voltammetry (CV). Figure 2 presents a comparison of the CVs obtained using (a) a bare GCE, and (b) the WO<sub>3</sub> NRc/GCE in phosphate buffer solution (PBS, 0.1M) at pH 7.0 and a scan rate of 50 mV/s.



*Figure 2. The CVs of (a) bare GCE and (b) WO<sub>3</sub> NR/GCE in the presence of 100.0 μM ACH in PBS (0.1 M, pH 7.0) and a scan rate of 50 mV s<sup>-1</sup>*

The CV of the bare GCE showed a weak oxidation peak for ACH in the studied potential range. Compared to the bare (unmodified) GCE, the WO<sub>3</sub> NRs/GCE exhibited significantly higher current responses and lower peak potential towards the oxidation of ACH. This enhanced electrochemical performance can be attributed to the improved specific surface area provided by the WO<sub>3</sub> NRs. The integration of the WO<sub>3</sub> NRs onto the electrode surface increased the effective surface area available for electrochemical reactions. This higher surface area allowed for more efficient electron transfer kinetics and redox processes compared to the bare GCE. These results indicate that modifying the electrode surface with WO<sub>3</sub> NRs/GCE can enhance the sensitivity and reduce the overpotential.

Figure 3 illustrates the impact of varying scan rates on the oxidation currents of ACH. Increasing the scan rate led to an enhancement of the peak currents. Moreover, the linear relationship between the peak currents ( $I_p$ ) and the square root of the scan rate ( $v^{1/2}$ ) suggests that the oxidation process is diffusion-controlled (Figure 3 inset).

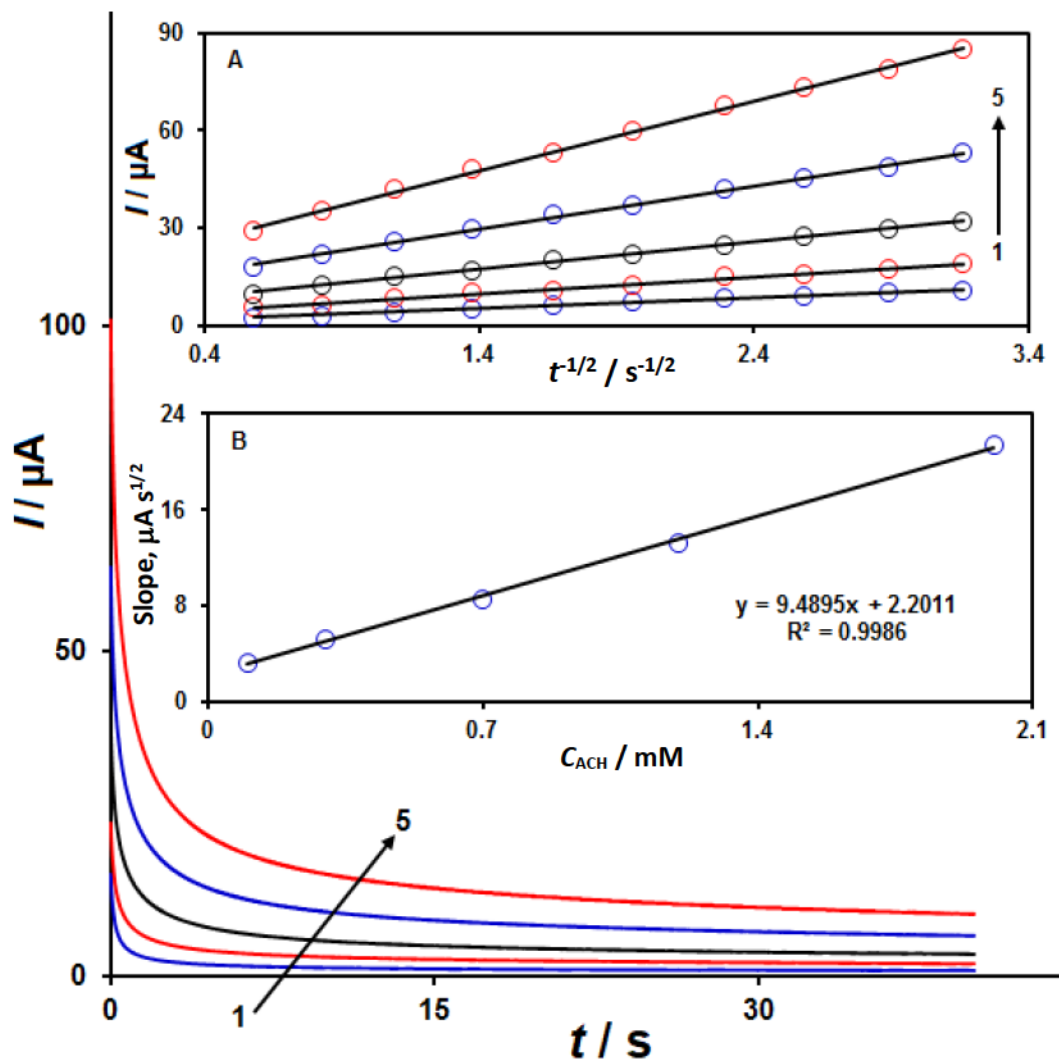


**Figure 3.** The CVs of a WO<sub>3</sub> NRs/GCE in PBS (0.1M, pH 7.0) containing 100.0 μM ACH at various scan rates (10 (1), 50 (2), 100 (3), 200 (4), 300 (5), and 400 (6) mV s<sup>-1</sup>). Inset: the variation of the anodic current as a function of the  $v^{1/2}$

#### Chronoamperometry studies

After the initial analysis of the CV data, a more in-depth investigation was conducted using the chronoamperometry (CA) method to determine the diffusion coefficient of ACH at the WO<sub>3</sub> NRs-modified electrode. Figure 4 presents a series of chronoamperograms obtained for ACH over the concentration range of 0.1 to 2.0 mM. These measurements were performed at a constant potential of 820 mV versus the Ag/AgCl reference electrode, which corresponds to the anodic oxidation of

ACH. Experimental plots of current versus the square root of time ( $t^{-1/2}$ ) were generated, and the best-fit lines were obtained for different concentrations of ACH (Figure 4, A). The slopes of these linear plots were then plotted against the ACH concentration (Figure 4, B). Using the Cottrell equation, the mean value of the diffusion coefficient ( $D$ ) was calculated from the slope of the plot in Figure 4B. The determined value of the diffusion coefficient was  $3.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ .



**Figure 4.** The chronoamperograms obtained at the  $\text{WO}_3$  NRs/GCE in PBS (0.1 M, pH 7.0) for different concentrations of ACH ((1) 0.1, (2) 0.3, (3) 0.7, (4) 1.2, and (5) 2.0 mM). Insets: (A) the plots of current versus  $t^{-1/2}$  obtained from the chronoamperograms and (B) the plot of slopes of the straight lines shown in (A) against the ACH concentration

#### Calibration curves

Figure 5 presents the differential pulse voltammetry (DPV) curves of the  $\text{WO}_3$  NRs/GCE with varying concentrations of ACH. As shown in Figure 5, the current of the DPV responses increases with the increasing concentration of ACH. The relationship between the current and the concentrations of ACH (0.1-400.0  $\mu\text{M}$ ) is exhibited in the inset of Figure 5. This linear relationship demonstrates the excellent sensitivity of the  $\text{WO}_3$  NRs/GCE sensor towards ACH. Furthermore, the LOD of the  $\text{WO}_3$  NRs-modified GCE for ACH was determined to be as low as 0.025  $\mu\text{M}$ . These results indicate that the  $\text{WO}_3$  NRs/GCE exhibits exceptional analytical performance, with a wide linear range and a remarkably low detection limit for the electrochemical determination of ACH. This highlights the potential of the developed sensor for practical applications.

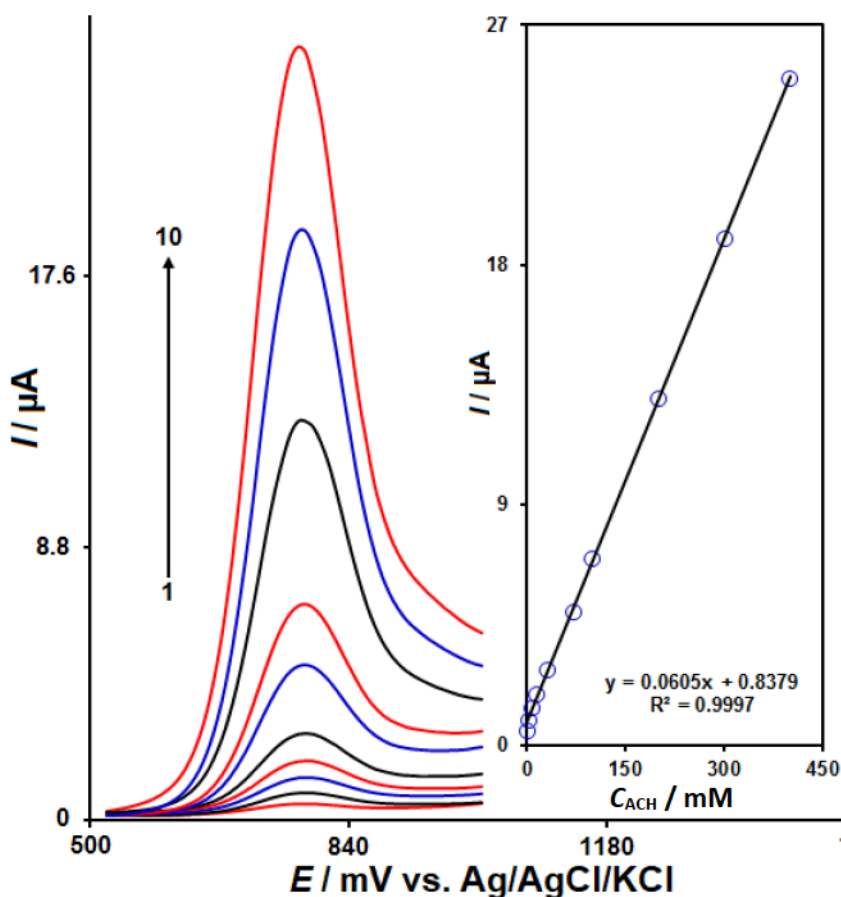


Figure 5. The DPVs of the WO<sub>3</sub> NR/GCE in PBS (0.1 M, pH 7.0) containing different concentrations of ACH (1) 0.1, (2) 2.5, (3) 7.5, (4) 15.0, (5) 30.0, (6) 70.0, (7) 100.0, (8) 200.0, (9) 300.0 and (10) 400.0 μM. Inset: the plot of the current as a function of the ACH concentration in the range of 0.1 to 400.0 μM

Real sample analysis

Urine samples were collected. The urine samples were then centrifuged at 2000 rpm for 15 minutes using 10 mL of the sample. The supernatant was filtered through a 0.45 μm filter. A certain volume of the filtered supernatant was then transferred to 25 mL volumetric flasks and diluted with 0.1 M PBS of pH 7.0 up to the mark. Different concentrations of ACH were added to spike the diluted urine and ACH tablet samples. The proposed electrochemical method was then used to analyze the ACH contents in the spiked urine samples and ACH tablets using the standard addition method. The results of this analysis are presented in Table 1.

Table 1. Determination of ACH on the WO<sub>3</sub> NRs/GCE surface in real samples (n = 5).

Sample	Concentration, μM		Recovery, %	RSD, %
	Spiked	Found		
ACH tablet	0	4.8	-	3.5
	1.0	5.7	98.2	2.8
	2.0	7.0	102.9	1.8
	3.0	7.7	98.7	2.2
	4.0	8.9	101.1	2.1
Urine	0	-	-	-
	5.0	5.1	102.0	2.3
	7.0	6.9	98.6	3.0
	9.0	9.1	101.1	2.1
	11.0	11.4	103.6	2.7

## Conclusion

This work presents a novel electrochemical platform for the quantitative determination of ACH using a GCE modified with WO<sub>3</sub> NRs. The electrocatalytic performance of the WO<sub>3</sub> NRs-modified GCE was investigated. The obtained results demonstrated favorable sensitivity, and precision in the detection of ACH. Under optimized conditions, the DPV signal exhibited a linear relationship between the oxidation current and the concentration of ACH, ranging from 0.1 to 400.0 μM. Importantly, a low LOD of 0.025 μM was achieved. This electrochemical probe was successfully employed to monitor ACH levels in ACH tablets and urine samples. The excellent analytical performance of the WO<sub>3</sub> NR-modified GCE highlights its potential for practical applications in the quantitative determination of ACH in various biological samples.

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