

*Full Paper*

## **A study of Electrocatalytic Activity of Ytterbium Tungstate Nanoparticles for the Determination of Nitrotriazolone**

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**Abstract-** In this work, chemical precipitation was used to form ytterbium tungstate nanoparticles ( $\text{Yb}_2(\text{WO}_4)_3$ ). This was achieved through the direct addition of a solution of ytterbium ions in water to that of tungstate. The structural and chemical properties of the prepared nanomaterial were evaluated by means of transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (XRD). The modified electrochemical electrode was prepared using synthesized ytterbium tungstate nanoparticles and electrochemical behavior of this electrode was investigated by electrochemical methods like CV, CA and DPV. Also, the effects concentration, pH and the potential scan rate were on the electrochemical process were investigated. It was found that the electrode modified with ytterbium tungstate nanoparticles enjoys excellent electrocatalytic activity for nitrotriazolone (NTO). The response of the electrode to NTO was linear in the concentration range of  $10^{-3}$  M to  $10^{-5}$  M, and the limit of detection in DPV analyses reached  $5 \times 10^{-6}$  M. Good performance for determination of NTO in water samples was obtained by DPV method.

**Keywords-** Nitrotriazolone, Ytterbium tungstate, Electrochemical, Sensor

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## 1. INTRODUCTION

Nano-sized materials have found to be effective in catalysis and photo-catalysis, and also in antibacterial agents, anti-parasitic agents, capacitors, sensing devices, and so on [1–8]. Among the different fields, modification of electrodes is a very appealing area in analytical chemistry [9–14], in which nanomaterials are among the promising candidates for use in enhancing the sensitivity and selectivity of these electrochemical devices [15–19]. One reason for this is the high surface areas of nanomaterials giving rise to enhanced signal/noise, mass transport and catalytic behaviors on the part of the modified device [20–25]. This is why various nanomaterials have been reportedly used in the construction of modified sensing and bio-sensing devices [26–30]. Lanthanide compounds have attracted a great deal of interest which arise from their 4f orbitals, which have a huge effect on their properties [31–35]. These rare earth elements have important peculiarities because their big number of electrons. Given the fact that f–f orbital transitions are laporte forbidden excited electrons return to the ground state at much slower rates as compared to d–d transitions, which is of special importance when tending to achieve the population inversion required for laser applications [36–37]. Ytterbium is a particularly interesting element because of its capacity to vary its valence under different conditions [38,39]. Furthermore, lanthanides tungstates are inorganics with great potential for use in phosphors, optical devices, magnets and catalytic compounds [40–43]. Rare earth tungstate can form various isomorphous structures with a general formula of  $RE_2(WO_4)_3$  some of which possess interesting characteristics [44]. Especially, ytterbium tungstate has excellent electrical, mechanical, and chemical stability and also have a good electrical conductivity; thus, it has been extensively investigated as optical and scintillator [45–47].

In the present work, ytterbium tungstate nanoparticles ( $Yb_2(WO_4)_3$ ) have been synthesized by facile, cost effective and rapid precipitation methods. For the first time, the synthesized ytterbium tungstate nanoparticles was employed as an electrocatalyst for the detection of nitrotriazolone (NTO). Compared to the unmodified electrode, the electrochemical behavior of NTO in the presence of ytterbium tungstate nanoparticles modified carbon paste carbon electrode has improved greatly leading to the develop a highly sensitive and stable sensor with good reproducibility and low detection limit for NTO.

## 2. EXPERIMENTAL

### 2.1. Apparatus and chemicals

Sodium tungstate, ytterbium (III) chloride, ethanol, graphite powder, sulfuric acid and phosphate salt (analytical grade) from Merck Co. were used without any pretreatment. A PGSTAT-302 Autolab potentiostat/galvanostat was used in the analyses. The waveforms and data acquisition were developed using the NOVA Autolab software. A three-electrode system composed of a normal or modified carbon paste electrode (CPE) as the working electrode

(WE), a platinum auxiliary electrode, and a reference electrode (Ag/AgCl/KCl (3.0 M)) was constructed and used for the analyses at ambient temperature. Initially the prepared samples were evaluated by SEM on a Philips XL30 instrument. For the purpose of the analyses the samples were coated with a gold film using a BAL-TEC SCD005 sputter coater.

## 2.2. Synthesis of ytterbium tungstate nanoparticles

Ytterbium tungstate nanoparticles were prepared by adding a 0.001 M solution of  $\text{Yb}^{3+}$  to a 0.005M solution of tungstate at  $40 \text{ mL min}^{-1}$  under stirring at  $30 \text{ }^\circ\text{C}$ . Once the reagents were fully mixed, the produced ytterbium tungstate was separated by filtration, repeatedly washed with water and then with absolute ethanol. The product was finally dried at  $80 \text{ }^\circ\text{C}$  for 4 h.

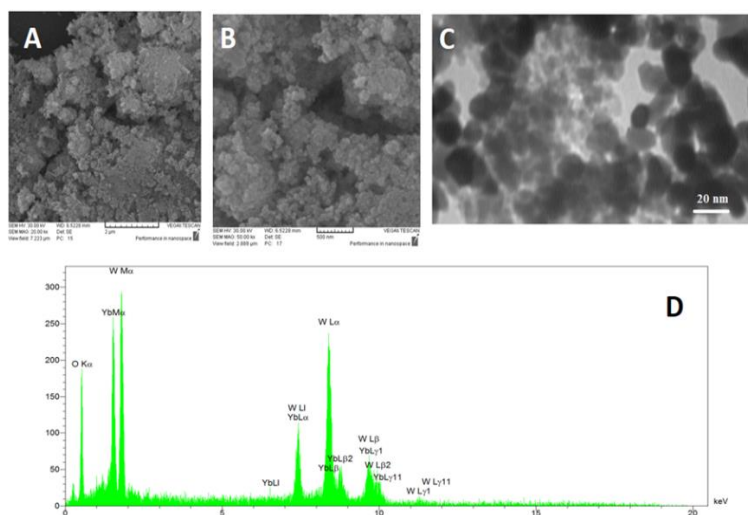
## 2.3. Modification of the carbon paste electrodes

0.304 g of graphite with 0.015 g of the ytterbium tungstate and 0.3 mL of paraffin was transferred into the sample container and mixed by stirring. To ensure uniformity and homogenization of the sample, some ethanol was added to the sample and then sample was completely mixed. After that, the sample was placed inside the oven to remove existing ethanol and obtain the desired carbon paste. The resulted modified carbon pastes were used as dough for the preparation of modified electrodes. The paste was compressed manually into a cavity (2 mm in diameter) located at the end of a 2 ml plastic syringe. At each time of using the pastes, after pouring the chosen paste on the oiled paper, the electrode surface was pulled to the dough to a sufficiently smooth surface. The electrical connection of carbon paste with the device was made through a copper wire which was inserted into the paste from the other opening of the syringe, and the resulting modified electrode (YW-CPE) was kept at ambient conditions in the dark.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization tests

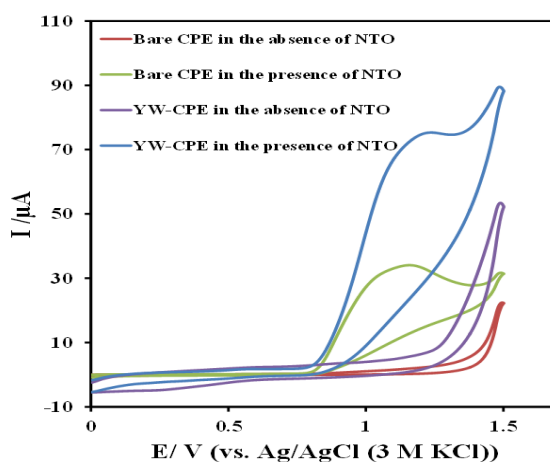
SEM results obtained for the product particles are presented in Fig. 1A and B. These images indicate that the nanoparticles are spherical and within a range of 30-35 nm in size. The TEM (Fig. 1C) image of the ytterbium tungstate nanoparticles supported these results (Fig. 1A) by indicating an average diameter of around 30 nm for the particles. EDS analyses (Fig. 1D) revealed the samples pure.



**Fig. 1.** SEM (A and B) and TEM; (C) of ytterbium tungstate nanoparticles synthesized via chemical precipitation reaction; (D) EDS spectrum of synthesized ytterbium tungstate nanoparticles by precipitation method

### 3.2. Electrocatalytic effect of yttrium tungstate on NTO oxidation

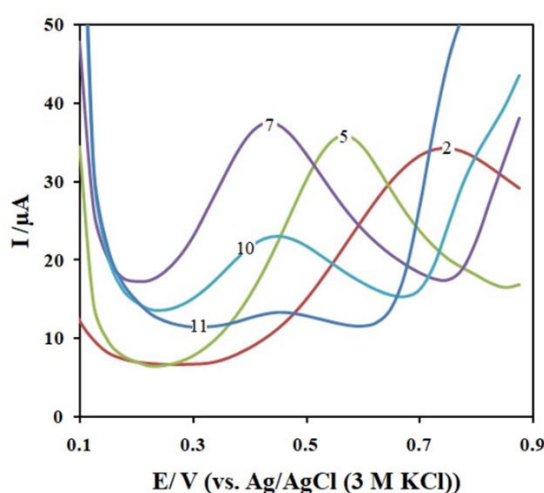
A bare CPE was first used to in a pure phosphate buffer solution (PBS, pH=7) and then in a 0.1 mM solution of NTO in the same PBS determine the concentration of NTO. Also, these steps were performed using a modified carbon paste electrode with ytterbium tungstate (YW-CPE). The total of the obtained voltammograms is shown in Fig. 2. The resulting voltammogram includes oxidation peaks of NTO when using bare CPE, while there was a significant increase in the anodic peak current could be observed, when using YW-CPE. It is clear that presence of the ytterbium tungstate nanoparticles enhances the behavior of the CPE in the presence of NTO in in PBS.



**Fig. 2.** Electrocatalytic effect of ytterbium tungstate nanoparticles on 0.1 mM NTO oxidation in phosphate buffer solution with pH=7

### 3.3. Influence of pH

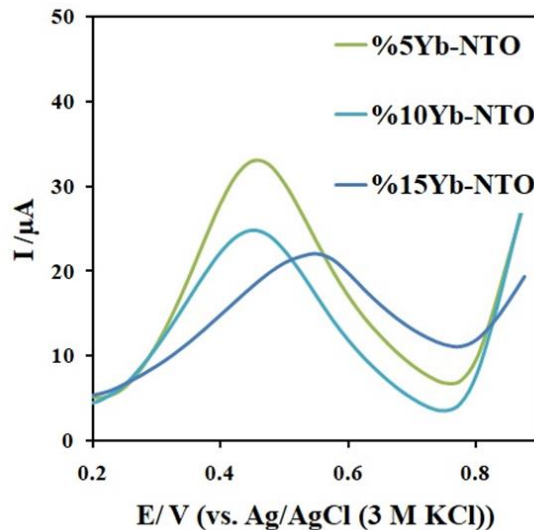
To investigate the influence of the pH of the solution on the response of the modified CPE, voltammograms of YW-CPE were obtained in solutions containing phosphate buffer 0.1 M and also containing NTO 1.0 mM with different pH values, as seen in Fig. 3. In acidic pH, YW-CPE have fewer currents in addition to having higher potentials than neutral and alkaline medium. Also, the stability of the electrode is strongly reduced in acidic pH and other interactions are observed in the resulting voltammograms. Furthermore, in alkaline pH, the peak potential remains constant, but its current decreases and it is not possible to measure at higher potentials due to unwanted reactions. Since the NTO has an acidic nature and can contribute in proton transfer reactions, hence working in alkaline pH conditions causes NTO to interact with the buffer solution and create other reactants [8]. Generally, potential of YW-CPE peaks is reduced with the increasing of pH, but the same peak potential is observed in the neutral and alkaline pH. The best value of peak current is also found at neutral pH. Based on the results, the optimal pH to be used for all other experiments was 7.



**Fig. 3.** The effect of pH on NTO oxidation at different pHs 2, 5, 7, 10 and 12

### 3.4. Effect of the percentage of ytterbium tungstate nanoparticles

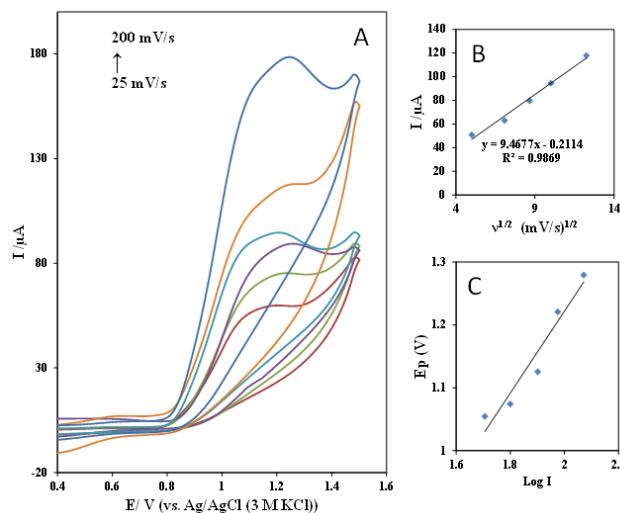
To investigate the effect of the percentage of ytterbium tungstate nanoparticles on the electrochemical oxidation of NTO, the voltammograms of YW-CPE with different ytterbium tungstate percentages in a 1 mM solution of NTO in 0.1 M PBS, which is seen in Fig. 4. Clearly, optimal percentage of modifier was 5% to measure NTO and peak current has dropped in high percentage of modifier.



**Fig. 4.** The effect of the percentage of ytterbium tungstate nanoparticles on the electrochemical behavior of the NTO oxidation, (a) 5% of the modifier, (b) 10% of the modifier, (c) 15% of the modifier

### 3.5. Influence of scan rate on NTO oxidation

The changes in the response of the YW-CPE with changing the potential scan rate was evaluated through CV experiments in a 0.1 mM solution of NTO in 0.1 mM PBS (pH=7.0). Fig. 5A shows a positive shift in the anodic peak potential as a result of increasing the scan rate, which reflects the fact that the reaction is a kinetically limited.

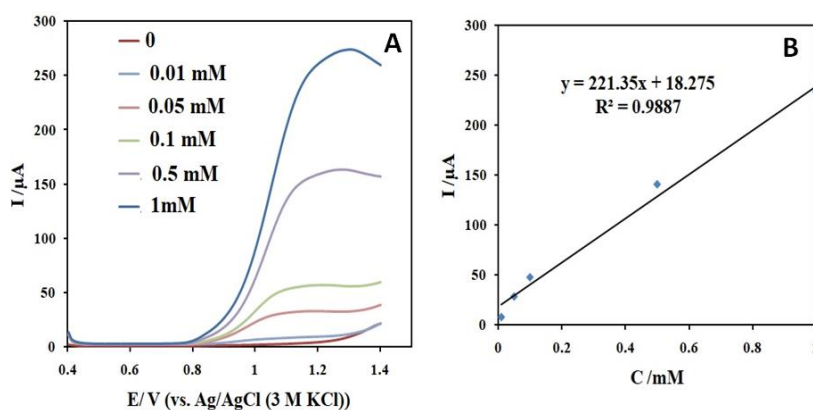


**Fig. 5.** (A) CVs curves of 0.1 mM NTO solution at YW-CPE in phosphate buffer solution for scan rates of 25, 50, 75, 100, 150, 200 mV/s, respectively; B) dependence of oxidation peak current on the square root of scan rate for different scans; C) plot of potential shifting versus the logarithm of scan rate

Fig. 5B, further shows that the changes in the oxidation peak current is a linear function of the square root of the scan rate. This reflects that the reaction is controlled by the rate at which NTO diffuses to the electrode surface, from the bulk of the solution. The slope of the plot of the peak potential against the logarithm of the scan rate (Fig. 5C) gives the TOEFL slope. This slope gives a transfer coefficient ( $\alpha$ ) of 0.64, considering the rate-determining step (RDS) to be a single electrode reaction.

### 3.6. Calibration curve and detection limit

The analytical properties of YW-CPE were studied by using it in DPV analysis of NTO concentration in PBS (pH=7) under optimal conditions (Fig. 6). As it can be observed, increasing the concentration of NTO shifted the peaks to in the more positive direction. The inset of Fig. 6 indicates the currents to be a linear function of NTO concentration from  $10^{-5}$  to  $10^{-3}$  M NTO. Using various NTO solutions in the range of  $10^{-5}$  to  $10^{-3}$  M, the limit of detection was determined as  $5 \times 10^{-6}$  M.



**Fig. 6.** (A) Linear concentration range for NTO by YW-CPE in phosphate buffer solution with pH=7 at various concentrations; B) Concentration calibration curve for NTO

### 3.7. Determination of NTO

The modified electrode was used in the analysis of NTO in tap water. The recovery data, indicate that the modified electrode is able to quantitatively recover into in water samples. The analyses involved spiking various amounts of NTO to water samples. Each sample was subjected to six replicate analyses using the sensor, and the recovery and precision results are given in Table 1. The results indicated that the presence of interfering species did not significantly influence the signal of the electrode to NTO. All recovery values ranged from 94.4–108.0%, indicating the applicability of YW-CPE to the direct detection of NTO in water samples.

**Table 1.** The obtained results from NTO measurement in real samples

sample	Amount added ( $\mu\text{M}$ )	Amount found	Recovery (%)	R.S.D. (n=6)
Water samples	25	23.6	94.4	3.6
	75	75.9	106	5.6
	250	270	108	4.7

#### 4. CONCLUSION

Nanoparticles of ytterbium tungstate were prepared through the direct addition of a solution of  $\text{Yb}^{3+}$  ytterbium to a tungstate solution in water. A modified carbon paste electrode based on ytterbium tungstate nanoparticles was used successfully for the determination of NTO. Based on obtained results, ytterbium tungstate nanoparticles improves the oxidation peak currents of NTO. The oxidation peak currents of NTO on YW-CPEs was a linear function of NTO concentrations from  $10^{-5}$  to  $10^{-3}$  M under optimal conditions and the detection limit was  $5 \times 10^{-6}$  M. The results indicated the good efficiency of the modified electrode for determining NTO in water samples. This results show the potential of ytterbium tungstate for construction of electrochemical sensor for determination of various analytes.

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