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# Chapter

# A Novel Electrochemical Sensor for the Detection of Reactive Red Dye to Determine Water Quality

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## Abstract

In this study, tragacanth gum/chitosan/ZnO nanoprism-based electrochemical sensors were prepared for sensing reactive dyes in water. To use an electrochemical sensor, a ~250 nm-sized ZnO nanoprism was synthesized via ultrasonic-assisted green synthesis method, using tragacanth gum and chitosan polymer blend as a matrix. The electrochemical properties of tragacanth gum/chitosan/ZnO nanoprisms were compared against reactive red 35, reactive yellow 15, and reactive black 194. The electrochemical measurement results indicated that prepared tragacanth gum/chitosan/ZnO nanoprism-based electrochemical sensor detected 25 ppm reactive red 35 in 1 min at room temperature. This study reveals new high-potential novel tragacanth gum/chitosan/ZnO nanoprism-based sensing material for the detection of reactive red dye-consisted wastewater with high sensitivity and short response time.

**Keywords:** ZnO, chitosan, nanoprism, electrochemical sensor, environmental monitoring, reactive dye, wastewater

## 1. Introduction

The physicochemical properties of nanomaterials make them suitable candidates for sensor applications due to their high surface area and surfactant functional groups. Nanomaterials with different morphologies help to adapt their application-specific detection properties. Therefore, researchers focus on effective detection platforms (reaction time, sensitivity, and selectivity) for the detection of aqueous reactive dyes based on different detection principles with sensors prepared with different morphological structures of nanomaterials (nanoparticles, nanowires, nanoprisms, etc.). Also, the materials in nanoscale exhibit higher dissolution and higher solubility than in microscale. Many types of nanomaterials such as metal oxide semiconductors, carbon-based nanomaterials, graphene/graphene-based nanomaterials, and metal-organic frameworks have been investigated for sensing reactive dyes in water [1–15].

Electrochemical sensing method involves the measurement of the redox transformation of reactive dye molecules upon contact with the sensing nanomaterial

surface. The method mainly consists of (a) conductometric/resistive, (b) amperometric/voltammetric, and (c) impedimetric electrochemical sensing. Voltammetric sensors work based on the current difference between reference and working electrodes. This approach utilizes the measurement of current as a function of variation in the applied potential difference in terms of the oxidation or reduction of an electroresponses of an electrochemical sensor. The peak current measured during voltammetry-mediated oxidation of analyte (e.g., reactive dye) is reflected as a function of its concentration. The sensitivity of the voltammetric electrochemical sensor is defined as $(I_g - I_0)/I_0$, where $I_g$ and $I_0$ are the currents while sensing film - analyte (e.g., reactive dye) is interacting and not, respectively. The voltammetric-type electrochemical sensing allows the quantification of the redox state of analyte in terms of current variations [16–18].

Transducers of the electrochemical sensors have attractive attention for preparing highly sensitive sensors. Nonuniform ohmic drop on an electrochemical transducer significantly affects the cyclic voltammogram data. The shape of the cyclic voltammograms predicts various electrochemical transducer geometries and experimental conditions [19–35].

Zinc oxide (ZnO) nanomaterials have distinct properties such as high sensitivity, high surface area, nontoxic, good compatibility, specific shape, nanosize, and correspondingly high isoelectric point. The unique and adjustable properties of ZnO nanomaterials as n-type semiconductor materials show excellent chemical and thermal stability in a wide range of applications such as solar cells, optical devices, sensors, etc. As far as the morphological perspectives of ZnO are concerned, the synthesis and production procedures also play an important role. The different parameters such as surfactant, temperature, concentration, and time are very significant for the growth of nanomaterials with different morphologies in various synthesis processes. Numerous different methods have been reported worldwide for the synthesis of ZnO nanopowder, composites, and films with good surface structure. Noteworthy techniques for the synthesis of various ZnO nanomaterials are generally deposition, wet chemical technique, sol-gel treatment, hydrothermal process, solvothermal process, and microwave techniques [36, 37].

This is the first report of the preparation and structural characterization of novel tragacanth gum/chitosan/ZnO nanoprism and investigation of the voltammetric electrochemical sensing characteristics of tragacanth gum/chitosan/ZnO nanoprisms against reactive dyes in water towards environmental monitoring. We suggest that this tragacanth gum/chitosan/ZnO nanoprism material has a great potential for future applications in high-performance, low-cost, portable, small-scale voltammetric electrochemical sensors towards forthcoming electronics.

## 2. Materials and methods

### 2.1 Materials

Tragacanth gum (T) and chitosan were purchased from Sigma-Aldrich Company. Reactive red 35 (RR35), reactive yellow 15 (RY15), and acid black 194 (AB194) were obtained from Burboya Company. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), glacial acetic acid (glacial 100%, pro analysis), and sodium hydroxide (NaOH) were purchased from Merck Company. MF-Millipore™ membrane filter was purchased from Merck Company. Ultrapure water was provided by a human ultrapure water system (water resistance: 18.3 Mohm) and was used for the preparation of all reactive dye solutions as analytes. All electrochemical gold transducers and voltammetric electrochemical workstation were purchased from Ebtro Electronics.
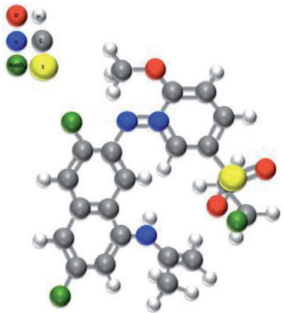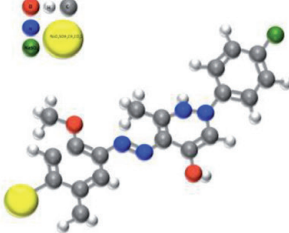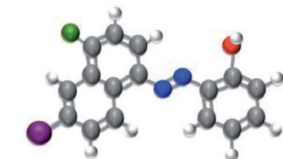
## 2.2 Synthesis of tragacanth gum/chitosan/ZnO nanoprism

Tragacanth gum/chitosan/ZnO nanoprisms were prepared using a green sonochemical method at 25°C (35 kHz frequency, 320 W, Sonoplus, Bandelin, Germany). In the first step, 0.1 g of tragacanth gum was dissolved in 50 ml of deionized pure water on a magnetic stirrer in 2 h at 25°C. In the second step, 0.1 g of chitosan was dissolved in 50 ml of 2% glacial acetic acid. In the third step, 25 ml of the prepared solutions was taken and mixed. In the fourth step, O.1 M of $Zn(NO_3)_2 \cdot 6H_2O$ and 0.2 M of NaOH was prepared in deionized pure water. In the fifth stage, the solution of $Zn(NO_3)_2 \cdot 6H_2O$ was added in the solutions, and then the solution of NaOH was added dropwise under the sonicator at 25°C for 40 min (%30 amp). The solution was kept at 24 h in the dark at room temperature. Then, it was first filtered through membrane filters of 0.45 μm and 0.22 μm pore size, respectively. The final solution (viscosity: 1.28 cP and pH 4) was stored at 25°C for use in the sterile container for analysis.

## 2.3 Preparation and measurements of electrochemical sensors

Electrochemical gold transducers were rinsed with ultrapure water, dried with nitrogen gas, and coated with tragacanth gum/chitosan/ZnO nanoprism solution by dropping and drying the solution. The 3D model structure and the property of dyes used are shown in **Figure 1**.

The potential of the working electrode was varied linearly with time, while the reference electrode was maintained at a constant potential. The potential was

| Dye | Molecular Formula | 3D model structure | Molar mass (g mol$^{-1}$) | λmax (nm) |
|---|---|---|---|---|
| Reactive Red 35 | $C_{12}H_{18}N_3Na_3O_{14}S_4$ | | 732.94 | 536 |
| Reactive Yellow 15 | $C_{20}H_{20}N_4Na_2O_{11}S$ | | 634.57 | 420 |
| Reactive Black 194 | $C_{20}H_{12}N_3NaO_7S$ | | 461.38 | 233 |

**Figure 1.**
*3D model structure and property of the reactive dyes.*

applied between the reference electrode and the working electrode, and the current was measured between the working electrode and the counter electrode. Ebtro voltammetric electrochemical workstation with a three-electrode configuration was used for all electrochemical tests. Cyclic voltammetry (CV) was performed in [−1, +1] V range with a scan rate of 50 mV/s.

## 3. Results and discussion

The structural analysis of the tragacanth gum/chitosan/ZnO nanoprism material was performed by X-ray diffraction (XRD) (**Figure 2**).

As seen in **Figure 2**, according to XRD analysis, strong peaks were observed at $2\theta = 13°, 31°$, which corresponds to the tragacanth gum/chitosan/ZnO crystalline planes. In the experiments, crystalline-structured tragacanth gum/chitosan/ZnO nanoprisms provided the advantage of obtaining a high surface area for higher interaction and reaction of sensing tragacanth gum/chitosan/ZnO nanoprism thin film on gold transducer-reactive dye with high electron mobility in terms of crystalline structure. SEM and EDX analyses of the prepared tragacanth gum/chitosan/ZnO nanoprisms were performed (**Figure 3**).

The EDX technique was employed to obtain some information on the spatial distribution of the corresponding elements. The EDX analysis of tragacanth gum/chitosan/ZnO nanoprisms provides the average percentage of zinc (Zn) and oxygen (O) at different points. All these suggest efficient preparation and presence of targeted atoms in tragacanth gum/chitosan/ZnO nanoprisms. The polymer matrix (tragacanth gum/chitosan) provides enormously large surface area for dispersion that helps ZnO to grow in the form of nanoprisms with higher reactivity for redox processing. The homogenous dispersion of ZnO in polymer matrix enhances conductivity and stability of the nanostructure. The complementary properties of tragacanth gum/chitosan/ZnO nanoprism generate a synergistic effect to enhance the electrochemical performance and provide improved charge exchange efficiency and stability during redox cycling.

Cyclic voltammetry measurements were performed to analyze the electrochemical sensor performance of tragacanth gum/chitosan/ZnO nanoprism-coated gold
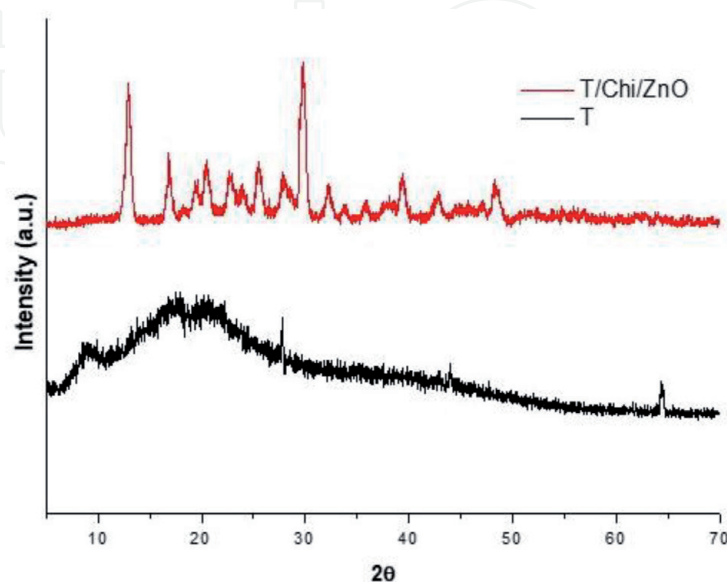


**Figure 2.**
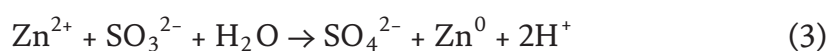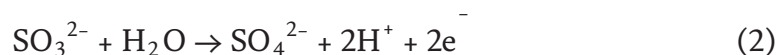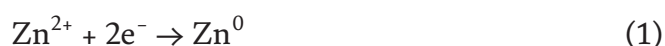*XRD analysis of tragacanth gum/chitosan/ZnO nanoprisms.*

(a)                                                        (b)
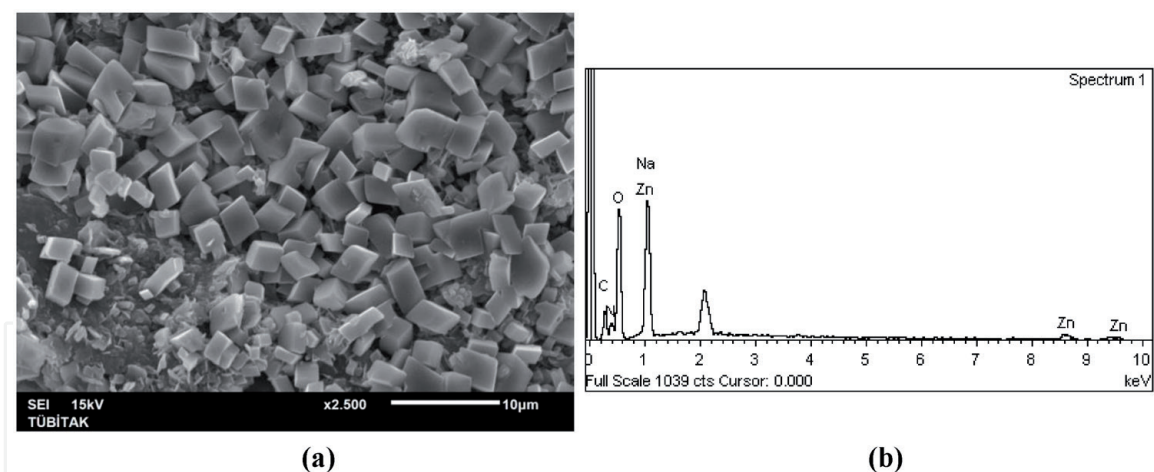
**Figure 3.**
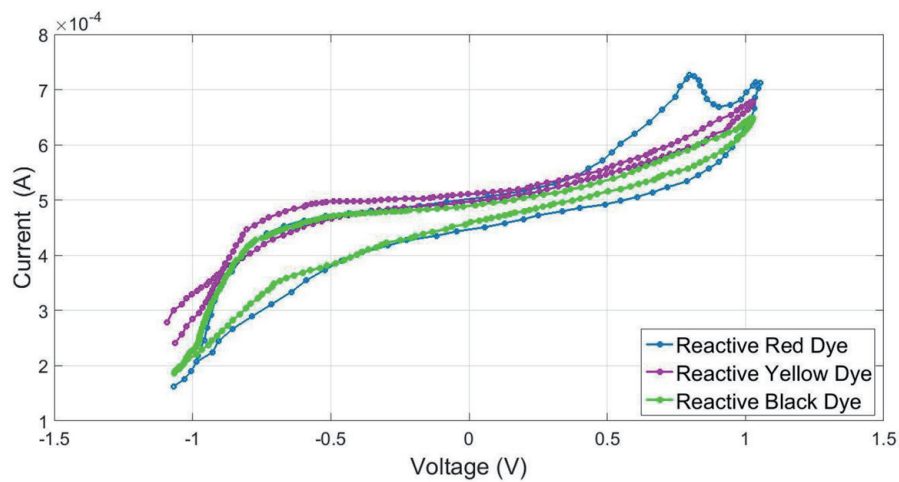*(a) SEM and (b) EDX analysis of tragacanth gum/chitosan/ZnO nanoprisms.*

transducer. Current-voltage curves of tragacanth gum/chitosan/ZnO nanoprism-coated gold transducers against reactive red 35, reactive yellow 15, and reactive black 194 were obtained, respectively, in [−1, +10] V range with a scan rate of 50 mV/s at room temperature in real-time measurements by Ebtro voltammetric electrochemical workstation (**Figure 4**).

**Figure 4** shows the comparative current-voltage curves of tragacanth gum/chitosan/ZnO nanoprism-coated gold transducers against reactive red dye, reactive yellow dye, and reactive black dye in [−1, +10] V range with a scan rate of 50 mV/s at room temperature. The measured current responses were due to either oxidation or reduction of the reactive dye analytes over the entire cycle at the surface of the bare gold transducers. The current peaks arised from redox reactions between tragacanth gum/chitosan/ZnO nanoprism and reactive red dye molecules observed. The curves showed that there are no peaks arising from reactive yellow and black dye molecules as redox reactions did not occur between tragacanth gum/chitosan/ZnO nanoprism and reactive yellow and black dye molecules. The goal of this research was to evaluate the performance of the tragacanth gum/chitosan/ZnO nanoprism-coated gold transducer of the voltammetric electrochemical sensor in discriminating different reactive dyes in water. In this context, we focused on the electrochemical sensing capability tragacanth gum/chitosan/ZnO nanoprisms against to reactive dye-consisted water. The electrochemical oxidation of reactive red dye-consisted water was observed using the scan rate of 50 mV/s at room temperature over a potential range of −0.2 to 0.8 V. In **Figure 4**, current-voltage curves of tragacanth gum/chitosan/ZnO nanoprism-coated gold transducer indicated a prominent redox peak for reactive red dye, while the other tragacanth gum/chitosan/ZnO nanoprism-coated gold transducers indicated no redox peak for reactive yellow and black dyes in water. The redox peak was attributed to a large number of $SO_3^-$ branches of the reactive red 35 (Eqs. (1)–(3)).

$$Zn^{2+} + 2e^- \rightarrow Zn^0 \qquad (1)$$

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^- \qquad (2)$$

$$Zn^{2+} + SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + Zn^0 + 2H^+ \qquad (3)$$

After these obtained results, sensor measurements were performed for determining reactive red dye. The different concentrations of reactive red dye were tested on tragacanth gum/chitosan/ZnO nanoprism-coated gold transducers in [−1, +10] V range with a scan rate of 50 mV/s at room temperature. Current peaks arised from redox reactions which came from between tragacanth gum/chitosan/ZnO nanoprism and reactive red dye molecules increased with increasing reactive red concentration in the range of 25–100 ppm. As the concentration of the reactive red dye molecules in the water increases, redox reactions increase the sensitivity of the sensor. Prepared tragacanth gum/chitosan/ZnO nanoprism-based electrochemical sensor detected 25 ppm reactive red dye in 1 min at room temperature.

The reproducibility of the tragacanth gum/chitosan/ZnO nanoprism-coated gold transducer was investigated by analyzing reactive red dye for four times. To ascertain the reproducibility results, the cyclic voltammetry experiments were carried out using the transducers under similar conditions. The peak currents for reactive red dye have not changed much even after a week. This showed the stability of the tragacanth gum/chitosan/ZnO nanoprism-coated gold transducer.



(a)
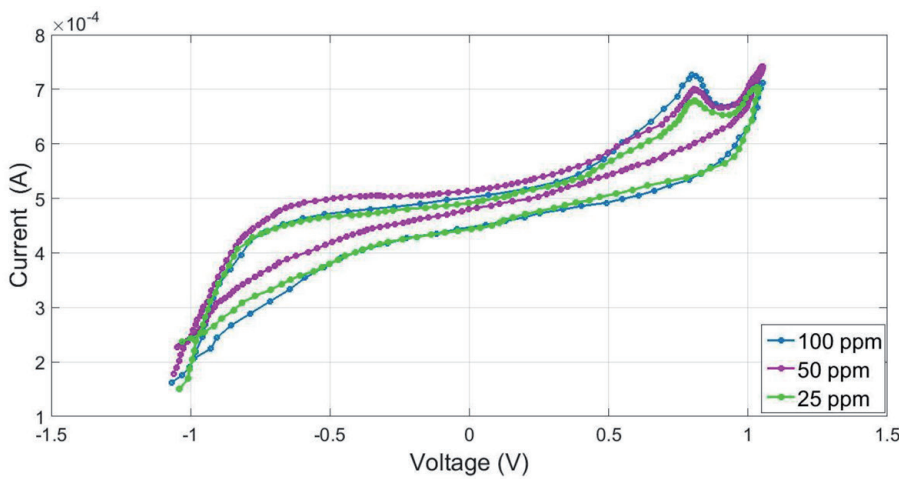


(b)

**Figure 4.**
*Current-voltage curves of tragacanth gum/chitosan/ZnO nanoprism-coated gold transducers against (a) reactive red dye, reactive yellow dye, and reactive black dye and (b) different reactive red dye concentrations in 25–100 ppm, [−1, +10] V range with a scan rate of 50 mV/s.*

## 4. Conclusions

In this study, for environmental monitoring of reactive dye-consisting wastewater, the novel tragacanth gum/chitosan/ZnO nanoprism-based electrochemical sensor was prepared and tested via cyclic voltammetry technique. The electrochemical measurement results indicate that prepared tragacanth gum/chitosan/ZnO nanoprism-based electrochemical sensor has a higher sensitivity against reactive red dye than reactive yellow dye and reactive black dye in water. Prepared tragacanth gum/chitosan/ZnO nanoprism-based electrochemical sensor detected 25 ppm reactive red dye in 1 min at room temperature. This study reveals new high-potential sensing material for the detection of reactive dye-consisting wastewater with high sensitivity and short response time. It is the first time that the sensing interaction of tragacanth gum/chitosan/ZnO nanoprisms and reactive red dye was explained.

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