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# Electrospun composite nanofibers of poly vinyl pyrrolidone and zinc oxide nanoparticles modified carbon paste electrode for electrochemical detection of curcumin

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ABSTRACT

A simple and novel ferrocene-nanofiber carbon paste electrode was developed to determine curcumin in a phosphate buffer solution at pH = 8. ZnO nanoparticles were produced via a sonochemical process and composite nanofibers of PVP/ZnO were prepared by electrospinning. The characterization was performed by SEM, XRD and IR. The results suggest that the electrospun composite nanofibers having a large surface area promote electron transfer for the oxidation of curcumin and hence the FCNFCPE exhibits high electrocatalytic activity and performs well in regard to the oxidation of curcumin. The proposed method was successfully applied for measurement of curcumin in urine and turmeric as real samples.



## 1. Introduction

Curcumin (CM) with the chemical name of (1E,6E)-1,7-bis (4-hydroxy-3-methoxyphenyl)-1,6-heptadiene 3,5-dione (Scheme 1) is known for its antitumor, antioxidant, anti-arthritic, anti-amyloid, anti-ischemic, and anti-inflammatory properties [1]. It fights free radical formations in blood and body tissues, effectively scavenging superoxide radicals [2], the hydroxyl radical and nitrogen dioxide among other reactive oxygen species [3]. Several mechanisms as antioxidant effect, inhibition of inflammatory factors, cell death induction and activation or inhibition of intracellular pathways that are involved in causing disease have been proposed for the pharmacological and biological effects of CM. CM has a significant role in preventing and treating cancer and numerous clinical studies have proven its effectiveness [4].

Because of the importance of CM, several methods, including liquid-liquid extraction [5], chromatography [6] and spectrophotometric methods [7], have been proposed for its determination in biological samples. Although these methods have been used successfully, they are time-consuming and need expensive equipment. Electrochemical methods, using chemical modified electrodes have been employed as a detection method for study of CM. Electrochemical sensors with nanofibers have received great attention owing to their high surface, good stability and unique electrochemical properties in the last decade [8]. Due to the small size of the electrospun polymer fibers, the membranes collected from these fibers possess a large surface area per unit mass and a very small pore size [9] and hence have many potential applications in optical materials [10], sensor materials [11], and nanocomposite materials [12], wound dressings, drug delivery systems [13], filtration and tissue scaffolds [14]. Fibers are usually produced by the traditional methods such as melt spinning, dry spinning and wet spinning [15]. Electrospinning has been developed to produce polymer fibers with sub micrometer or nanometer diameters [9]. Compared to most other methods, electrospinning has a simple yet versatile setup that produces a significant amount of ultrafine fibers in a short period of time [16]. Other advantages include ease of room temperature deposition, synthesis of continuous, uniform nanofibers and making a wide range of precursor materials available for synthesis [17]. Morphology of the nanofibers can be controlled by viscosity, surface tension, and the density of net charges of the solution [18].

Zinc oxide (ZnO) is an II–VI semiconductor with a wide and direct band gap of about 3.37 eV (at 300 K). It has a large excitation binding energy of 60 meV, high mechanical and thermal stabilities and radiation hardness [19]. The nanoparticles of zinc oxide have applications in solar [20], semiconductors [21], gas sensors [22], catalysis [23], varistors [24], thermoelectric [25], pharmaceutical and cosmetic industries [26].

Ultrasonic irradiation has been widely used in the solution phase processes of the recent ZnO nanostructure synthesis techniques, such as chemical vapor deposition [27], thermal evaporation [28] and sputter deposition [29].

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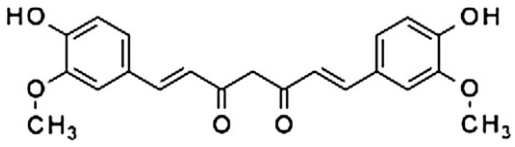

**Scheme 1.** The structure of CM.

In this study we utilized a modified carbon paste electrode (MCPE) fabricated by mixing the electrospun composite nanofibers of PVP/ZnO with ferrocene (FC), hence resulting in a high sensitive sensor for voltammetric determination of CM in PBS (pH = 8). The dependence of oxidation peak current on pH of the solution and scan rate were studied to optimize the experimental conditions for electrochemical determination of CM. This ferrocene-nanofiber carbon paste electrode (FCNFCPE) exhibited attractive analytical performance, such as low detection limit, wide linear range and high sensitivity for determination of CM and could be used as a simple sensor in the analysis of CM in the human urine and turmeric samples.

## 2. Materials and methods

### 2.1. Chemicals

Poly vinyl pyrrolidone (PVP, Mw 25,000 g $mol^{-1}$), zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), diethylene glycol ($O(CH_2 \cdot CH_2OH)_2$) and FC were purchased from Sigma Aldrich. CM was purchased from Merck and the required concentration was prepared by using pure ethanol (99%). All electrochemical studies were performed in phosphate buffer (pH = 8) using $Na_2HPO_4$ and $NaH_2PO_4$. The pH was adjusted by using NaOH. All the aqueous solutions were prepared using doubly distilled water.

### 2.2. Preparation of ZnO nanoparticles

For the ultrasonic synthesis, 10 mL of 0.5 M zinc acetate dihydrate solution was irradiated in the presence of diethylene glycol with an ultrasonic probe (TopSonics UPH-400, ultrasonic technology development Co.) on 15 s pulse mode (8 s on and 7 s off) at room temperature. The mixture was centrifuged and the sediment was washed three times with distilled water and ethanol. The product was dried at 80 °C for 12 h. Some process parameters such as effect of surfactant and irradiation intensity and time were evaluated. The optimized parameters are shown in Table 1. The size and morphology of the synthesized nanoparticles were studied using an EM 3200 scanning electron microscope (SEM) at 26 kV accelerating voltage (Kyky, China). The structural properties of the ZnO nanoparticles were characterized by X-ray diffraction using the Xpert MPD diffractometer (Philips, Netherlands) and the Bruker Tensor 270 infrared spectroscope.

### 2.3. Fabrication of composite nanofibers of PVP containing ZnO nanoparticles

The 16% w/v polymeric solution of PVP was prepared in ethanol and placed in an ultrasonic bath to obtain a viscous and homogeneous solution. A 1% wt. nanoparticles suspension was also prepared in methanol simultaneously. Then the polymeric solution and nanoparticles suspension were transferred into two separate syringes with an inner diameter of 12.96 mm and a two axial needle with internal axis of 17 gauge (0.203 mm diameter) and external axis of 18 gauge (0.216 mm diameter). An aluminum foil was placed on the collector at a distance of 100 mm from the tip and the process was operated under an applied voltage of 25 kV and solution injection rate of 0.5 mL/h [30]. The experimental apparatus used for electrospinning was from Fanavaran Nano Meghyas (Fnm-ES1000) (Tehran, Iran). A high voltage electric field for electrospinning process was produced by a high voltage power supply (DC-high voltage generator, HV35P OV). Table 2 shows the optimal electrospinning process parameters.

**Table 1**
Sonochemical conditions to produce ZnO nanoparticles.

| Parameters | Values |
|---|---|
| Irradiation intensity (W) | 150–200 |
| Irradiation time (min) | 11–24 |
| Temperature (°C) | 21 ± 4 |

### 2.4. Preparation of FCNFCPE

The modified carbon paste was made by hand mixing of 0.89 g graphite powder, 0.01 g FC, as diffusional electron mediator, 0.1 g nanofibers, as reformer and 0.7 mL of silicon oil. The MCPE was constructed by packing this paste into a glass tube (inner diameter 3 mm and length 10 cm) and the surface of the electrode was lightly polished with weighing paper. The electrical contact was provided by a copper wire. Other electrodes including CPE with FC electron mediator (in the absence of nanofibers), CPE modified with nanofibers (in the absence of FC) and CPE (in the absence of FC and nanofibers) were prepared by the same procedure and used for comparative experiments. Electrochemical measurements were performed using the VA Computrace 757 electrochemical analyzer (Metrohm, Switzerland) equipped with a standard 3-electrode cell. The auxiliary electrode was a Platinum wire. A saturated Ag/AgCl electrode was used as a reference and modified CPE was utilized as the working electrode. The pH of the solutions was adjusted by a model 713 pH Lab Metrohm Swiss meter.

### 2.5. Preparation of real samples

10 mL urine sample was centrifuged for 15 min at 2000 rpm. The supernatant was filtered with a 0.45 μm filter and was diluted with PBS (pH = 8.0).

In order to prepare turmeric powder for CM extraction, 0.24 g of turmeric powder was dissolved in 12 mL of ethanol and centrifuged at 120 rpm. Then supernatant solution was filtered and used for next operation.

## 3. Results and discussion

### 3.1. Effects of sonochemical process parameters on the ZnO nanoparticles size and morphology

#### 3.1.1. Effect of ultrasonic irradiation intensity

To study the effect of ultrasonic irradiation intensity in the process, the solution was irradiated at the intensity of 150–200 W. Fig. 1 shows the SEM images of ZnO nanoparticles produced under different conditions. Fig. 1(a–b) show the structure of ZnO nanoparticles synthesized in the presence of diethylene glycol as surfactant with the irradiation intensity and time of 200 W and 20 min. Fig. 1b clearly indicates

**Table 2**
Electrospinning parameters for production of PVP/ZnO composite nanofibers.

| Parameters | Values |
|---|---|
| Polymer solution concentration (%w/v) | 16 |
| Nanoparticles suspension concentration (%w/w) | 1 |
| Electric voltage (kV) | 25 |
| Electrospinning distance (mm) | 100 |
| Capillary diameter (mm) | 12.96 |
| Solution injection rate (mL/h) | 0.5 |
| Collector speed (rmp) | 1000 |
| Temperature (°C) | 30 ± 4 |
| Internal axis diameter of needle (mm) | 0.203 |
| External axis diameter of needle (mm) | 0.216 |