

Experimental study of the effect of undoped ZnO, Fe and Mn doped ZnO nanostructures and the electrochemical response of the nanostructures modified carbon paste electrode toward Levodopa

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Abstract

In this study, undoped ZnO, Fe and Mn doped ZnO nanostructures were synthesized by hydrothermal method. The morphology of nanostructures was characterized by Scanning Electron Microscope. The electrochemical response of the carbon paste electrode modified with nanoparticles of ZnO and also ZnO doped with Fe and Mn toward levodopa (L-Dopa) was studied. Studies of cyclic voltammetry using provided modified electrode showed electro catalytic properties for electro-oxidation of L-Dopa, and a significant reduction in anodic over voltage compared to bare electrode was observed. Best response was obtained in terms of the current enhancement, overvoltage reduction, and reversibility improvement of the L-Dopa oxidation reaction under experimental conditions by modified electrode with zinc oxide nanoparticles doped with iron.

Keywords: ZnO; hydrothermal method; Levodopa analysis; modified electrode; doping; Fe; Mn.

Introduction

Nanotechnology is the manipulation of matter at the atomic scale materials and

devices by controlling the scale of a billionth of a meter. The different nanostructures such as zinc oxide, due

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to its electrical conductivity and high transparency, have widespread applications in electronics, solar cells, gas sensors and modified electrode preparation [1].

ZnO is a well-known wide direct band gap (3.2 eV at room temperature) and high exciton binding energy (~ 60 meV) semi conducting material. ZnO is an II–VI semiconductor with properties similar to GaN. It is therefore a potential candidate for optoelectronic applications in the short wavelength range (green, blue, UV), information storage and sensors [2-8].

It is well known that the size, type of composition and morphology of ZnO semiconductor have great influences on its sensing properties. Up to date, different morphologies, sizes and composites of ZnO materials have been successfully synthesized, including nanotetrapods with hexagonal crown [9], nanoflower [10], nanorod [11], nanotube [12], star-like [13], etc.

L-Dopa is a medication used to treat Parkinson's disease. This type of disease is associated with low levels of dopamine in the brain. L-Dopa is turned into dopamine in the body and therefore increases levels of this chemical. Also, L-Dopa is used to treat

the stiffness, tremors, spasms, and poor muscle control of Parkinson's disease. L-Dopa is also used to treat these same muscular conditions when they are caused by drugs such as chlorpromazine, fluphenazine, perphenazine, and others [14].

Materials in nanosize such as graphene, type of carbon nanotubes, nanoparticles and nanocomposite have also been incorporated into the modified electrode as a voltammetric sensor in the recent years [15–23].

In this paper, we synthesize undoped ZnO, and also ZnO doped with Mn and Fe nanostructures by hydrothermal method at low temperature. We describe the preparation and application of a FeZnO/CPE, MnZnO/CPE, ZnO/CPE as a new sensor for the investigation of the electrochemical behavior of L-Dopa and report a simple low temperature hydrothermal method for preparation of ZnO, Mn and Fe doped ZnO.

Experimental

Chemicals and apparatus

Graphite fine powder, paraffin oil and all other chemicals were purchased from Merck. All the electrochemical measurements were performed at 25 ± 2 °C with a three electrode assembly,

including an Ag/AgCl electrode as the reference electrode and a platinum wire as the counter electrode. The working electrode was either an unmodified carbon paste electrode (CPE), or MnZnO/CPE, ZnO/CPE and FeZnO nanorods modified carbon paste electrode (FeZnO/CPE).

A 100 μ M L-Dopa solution was prepared daily by dissolving 0.01 g of L-Dopa (from Merck) in water and the solution was diluted to 50 mL with water in a 50 mL volumetric flask. The solution was kept in a refrigerator at 4 °C in the dark container. More dilute solutions were prepared by serial dilution with buffer solution.

Phosphate buffer solutions (PBS) with pH=2 was used. A SAMA 500 electrochemical work station (SamaInstruments, Iran) equipped with a personal computer was used for electrochemical measurements and data analysis. The SAMA software was used for control and data acquisition.

General synthesis of ZnO, Mn and Fe doped ZnO

For preparation of pure ZnO, 5 mmol Zn(CH₃COO)₂·2H₂O was dissolved in 50 mL distilled water at 20±2°C temperature with vigorous stirring for 30 min. Then, 10 mmol sodium

hydroxide (NaOH) powder was added under stirring and the solution was transferred to an autoclave and kept at 90 °C in oven for 2 h. After completion of the reaction, white colored product was filtered and washed with double distilled water until freed from impurities. Finally, the obtained product was calcined at 400 °C for 2 h.

Mn and Fe doped ZnO were prepared by the same hydrothermal method and the concentration of these dopants (FeCl₃·6H₂O or MnCl₂·6H₂O) was 1.0 mol % (mole ratio of dopant to Zn is 0.01).

General preparation of modified electrode

Modified carbon paste electrode was prepared by thoroughly hand-mixing as 1mg of undoped ZnO, Mn and Fe doped ZnO which were dispersed in 1 mL ethanol by an ultrasound bath for 30 minutes to get a homogeneous dispersion. Prior to the use, a mirror-like surface was obtained by polishing the electrode on a weighing paper. Then 2 μ l of the suspension was casted on CPE surface and dried at the room temperature. The resulted electrode was denoted as ZnO/CPE. At the same time, 1 mg/mL Mn doped ZnO ethanol suspension solution and 1 mg/mL Fe

doped ZnO ethanol suspension solution were prepared and casted on CPE surface to get MnZnO/CPE and FeZnO/CPE, respectively.

General recommended procedure

The new surface can be obtained by pushing an excess of paste out of the tube, removing the excess, and polishing again mechanically the electrode surface. Also bare CPE in the absence of MnZnO and FeZnO were prepared in the same way, and for comparison, undoped ZnO modified CPE electrode (ZnO/CPE) was prepared by adding the appropriate amount of undoped ZnO to the bare carbon paste electrode. Therefore, ZnO/CPE, MnZnO/CPE, FeZnO/CPE were polished with a white and clean paper. The initial and final potentials were adjusted to 0.1 and 0.8 V vs. Ag/AgCl, respectively. Calibration curve was constructed by plotting the anodic peak current vs. the L-Dopa concentration.

Results and discussion

Characterizations of the prepared undoped ZnO, Mn and Fe doped ZnO

The morphologies of undoped ZnO and doped with Mn and Fe nanostructures are shown in Figure 1.

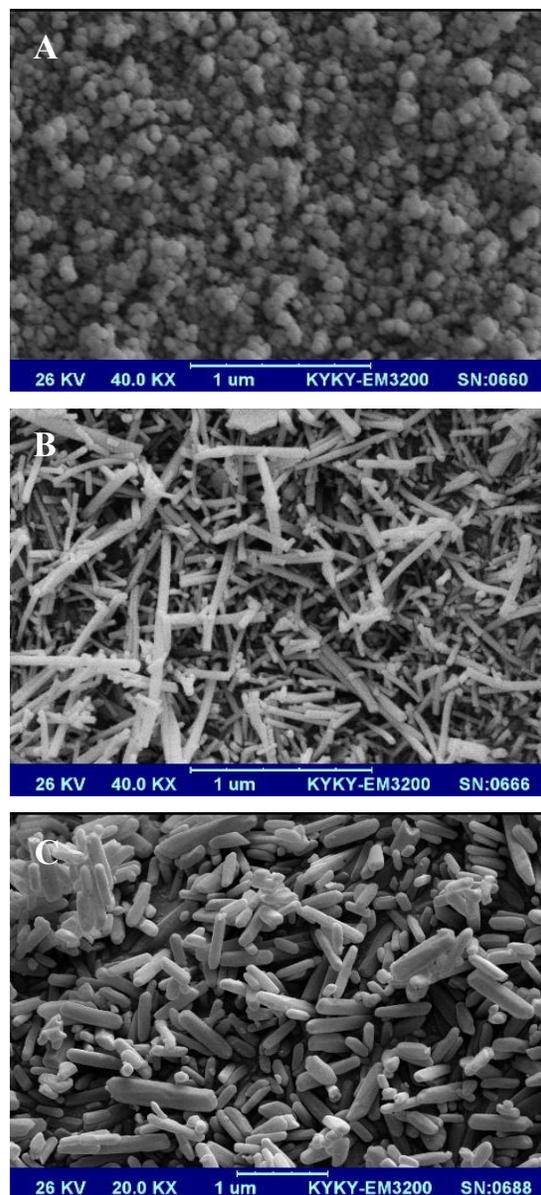


Figure 1. SEM image of (A) ZnO nanoparticles (B) Fe doped ZnO and (C) Mn doped ZnO

The average grain size of undoped ZnO, Fe and Mn doped ZnO particles were 56, 49 and 86 nm, respectively. It is clear that Mn and Fe dopant ions in the host ZnO lattice caused to change the morphology of ZnO nanoparticles

to nanorods. It was reported that the morphology of nanorods strongly depends on various parameters, such as the synthesis method, growth temperature and precursor concentration [24-26]. Xu *et al.* have reported diameter reduction for Cu doped ZnO nanorods synthesized by the hydrothermal method from 100 nm to 70 nm due to increase of Cu concentration from 0% to 1.5% [27]. Murugadoss *et al.* doped ZnO nanorods with different transition metals such as Mn, Co and Ni and observed crystal quality of the ZnO nanorods noticeably decreased by the impurity [28]. The above results demonstrate that Mn and Fe doping could strongly affect the structural characteristics of nanostructures due to the difference of ionic radius between Zn, Mn and Fe ions.

Electrochemical characterizations of the modified electrode

The cyclic voltammograms of CPE, ZnO/CPE, MnZnO/CPE and FeZnO/CPE in 0.1 M phosphate buffer

solution (pH = 2.0) containing 100 μ M L-Dopa were obtained. When the undoped ZnO nanoparticle was added into CPE, the redox peaks currents increased obviously. With adding the MnZnO and FeZnO nanorods into CPE, the decrease of ΔE_p (346 and 132 mV) and the increase of the peak current were observed which could be attributed to the high surface area of MnZnO and FeZnO nanorods, leading to an increase in the electron transfer between the analyte and the electrode surface.

Voltammetric behavior of L-Dopa

Figure 2 and 3 show voltammetric responses of 100 μ M L-Dopa in 0.1 M PBS (pH = 2.0) on different modified electrodes. No redox peak was observed on modified CPEs in blank PBS, Figure 2C, indicates that the modified CPEs were stable in the selected potential region without any redox reaction. The redox peak currents and potentials of L-Dopa on different modified electrodes were recorded and listed in Table 1.

Table 1. Cyclic voltammetric results of 100 μM L-Dopa on different modified electrodes

Electrodes	I_{pc} (μA)	I_{pa} (μA)	E_{pc} (V)	E_{pa} (V)	ΔE_p (V)
CPE	-3.9	5.6	0.263	0.674	0.411
ZnO/CPE	-6.7	7.7	0.323	0.620	0.297
MnZnO/CPE	-3	3.7	0.487	0.552	0.065
FeZnO/CPE	-7.4	9.8	0.329	0.608	0.279

It can be seen that a pair of redox peaks were appeared on the modified electrodes with the improvement of the voltammetric responses, which was due to the modification of nanomaterials step-by-step and the results indicated that the electro-oxidation of L-Dopa was took place and accelerated on the modified electrodes. Preliminary studies were conducted in order to determine the optimal catalytic activity compared to electro-oxidation of L-Dopa by synthesized Zinc oxide nanoparticles and doped samples with cyclic and differential pulse voltammetry method. Voltammetric response of L-Dopa was investigated at the surface of unmodified carbon paste electrode (CPE) and modified carbon paste electrode with the synthesized nanoparticles. Recorded cyclic voltammograms in 0.1 M PBS pH=2 containing 100 μM L-Dopa with a potential sweep rate of 100 mVs^{-1} were shown in Figure. 2A. At the surface of

CPE, an anodic peak with peak potential of 674 mV and a cathodic peak with peak potential of 263 mV for L-Dopa is observed. Potential difference of oxidation-reduction peaks was obtained equal to 411 mV which expresses its irreversibility at the surface of unmodified electrode. Oxidation-reduction peak potentials of L-Dopa on CPEs modified with nanoparticles of zinc oxide and doped zinc oxide nanoparticles with iron were shifted respectively to 620 and 608 mV for oxidation and 323 and 329 mV for reduction.

Notably, the results of differential pulse voltammetric, Figure 2B, confirmed obtained results by CV method. On the other hand, on the modified electrodes, redox peak currents show a significant increase. Based on these observations, it can be concluded that importing modifier nanoparticles indicated an effective catalytic model in redox reaction of L-

Dopa leading to reduction in over-voltage and a significant increase in redox currents.

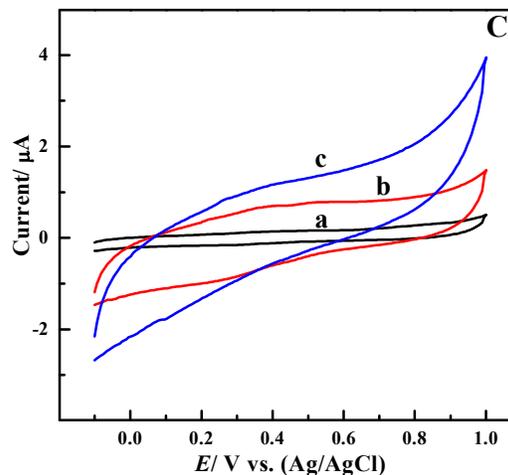
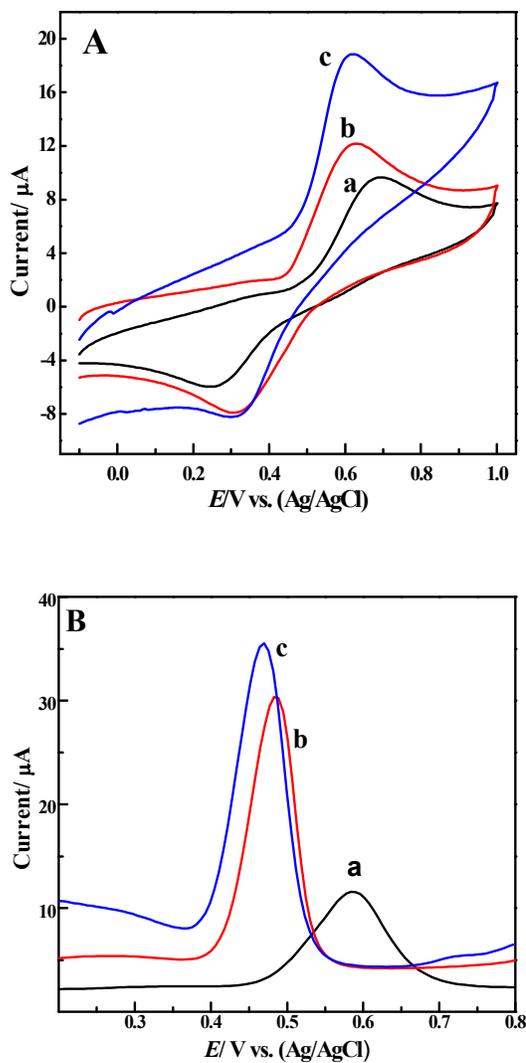


Figure 2. (A) Cyclic voltammograms (CVs) and (B) the differential pulse voltammograms (DPVs) of 100 μM L-Dopa on different electrodes. (C) CVs in blank PBS. Bare CPE (black line, a) and electrodes modified with ZnO (Red Line, b) and Fe-ZnO (blue line, c) nano-rods in 0.1 M PBS pH = 2.0 with the potential scan rate 100 mVs^{-1} and pulse amplitude 50 mV.

Figure 3 shows voltammetric responses of 100 μM L-Dopa in 0.1 M PBS (pH = 2.0) on MnZnO/CPE. Obviously, redox peaks in this case were weaker than those obtained on the surface of FeZnO/CPE.

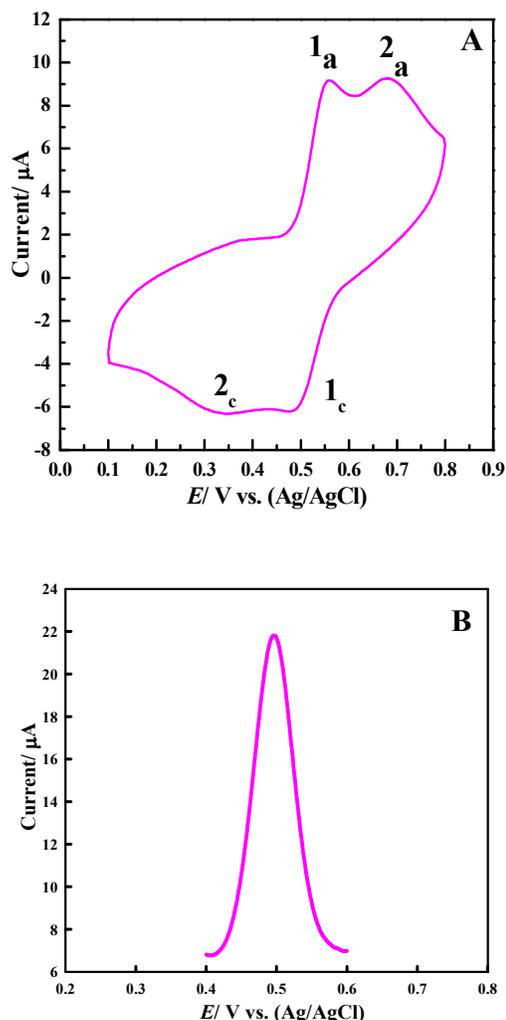


Figure 3. (A) CV and (B) DPV of 100 μM L-Dopa in 0.1 M PBS pH = 2.0 on Mn-ZnO/CPE, the potential scan rate 100 mVs^{-1} and pulse amplitude 50 mV.

In the case of MnZnO/CPE, two redox peaks were observed. Notably, MnZnO suspension was not homogeneously covered the CPE surface. Therefore, both of the bare CPE and CPE covered with thin layer of MnZnO were in contact with analyte

solution. The redox peaks (1a-1c) were related to parts of CPE covered with MnZnO/CPE while the redox peaks (2a-2c) were related to bare sections of CPE. Obviously, MnZnO can be considered as a suitable modifier for L-Dopa oxidation if stable suspension is prepared and casted as a homogeneous thin film on the surface of bare CPE.

Comparison between the electrochemical oxidation of L-Dopa on the surface of three different modified electrodes indicated that the best catalytic activity to reduce the overvoltage of electrode process and sharpness improvement and redox peak current was obtained by the modified electrode with zinc oxide nanoparticles doped with iron.

Conclusion

In summary, undoped ZnO nanoparticle, FeZnO and MnZnO nanorods were synthesized successfully by a simple low temperature hydrothermal method. Electrochemical behaviors of L-dopa on ZnO/CPE, MnZnO/CPE and FeZnO/CPE were carefully investigated with the electrochemical parameters calculated. The results show that the oxidation peak current of L-dopa was increased obviously on FeZnO/CPE. High

sensitivity and good repeatability of the voltammetric responses were observed. In addition, the FeZnO modified CPE had good reproducibility and could be applied to determination of L-dopa in samples with satisfactory results.

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