Microchemical Journal 130 (2017) 205–212

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Synthesis of nickel nanowrinkles and its application for the electrocatalytic oxidation and sensitive detection of hydrochlorothiazide

H. Heli [a,*], J. Pishahang [b,c], H. Barzegar Amiri [b,d], N. Sattarahmady [a,e,**]

[a] Nanomedicine and Nanobiology Research Center, Shiraz University of Medical Sciences, Shiraz, Iran
[b] Central Laboratory of Jam Petrochemical Complex, South Pars Special Economy and Energy Zone, Assaluye, Iran
[c] Department of Chemistry, Lamerd Branch, Islamic Azad University, Lamerd, Iran
[d] Department of Chemistry, Faculty of Science, Payame Noor University, Assaluyeh, Iran
[e] Department of Medical Physics, School of Medicine, Shiraz University of Medical Sciences, Shiraz, Iran

ARTICLE INFO

Article history:
Received 4 April 2016
Received in revised form 6 July 2016
Accepted 15 September 2016
Available online 16 September 2016

Keywords:
Nickel
Nanowrinkles
Hydrochlorothiazide
Hydrothermal synthesis
Electrocatalysis

ABSTRACT

Nickel nanowrinkles were synthesized by a simple hydrothermal method in one step in the presence of fluoride ions in ethylene glycol. The nanowrinkles were then employed as the modifier of a carbon paste electrode. The kinetics of the charge transfer across the modified electrode/solution interface was studied and the modified electrode was employed to fabricate an amperometric sensor of hydrochlorothiazide. The mechanism and kinetics of the electrocatalytic oxidation of hydrochlorothiazide on the modified electrode surface were studied by cyclic voltammetry and chronoamperometry. An amperometric procedure was developed for determination of hydrochlorothiazide with a sensitivity of 13.50 mA mol^{-1} dm^3 cm^{-2} and a limit of detection of 21.2 μmol dm^{-3}. The method was used for the direct assay of hydrochlorothiazide in human serum samples and hydrochlorothiazide tablets. The sensor had the advantages of sensitivity (guaranteed by a Nafion layer on the sensor surface), high electrocatalytic activity and long-term stability toward hydrochlorothiazide.

1. Introduction

Analysis of drugs and pharmaceuticals has an extensive impact on public health. Amperometry and voltammetry can be employed as convenient alternatives to the routine methods of analysis. Electroanalytical methods permit direct, simple and rapid determination without, in most instances, derivatization, requiring a minimum volume of sample, having been used for determination of a wide range of drugs [1]. In addition, knowledge of redox properties of drugs can provide insight into their metabolic fate, their in vivo processes, and their pharmacological activity [2–5].

Hydrochlorothiazide (6-chloro-3,4-dihydro-2H-1,2,4-benzothiadiazine-7-sulfonamide 1,1-dioxide, HCT, Scheme 1) is a benzothiadiazine diuretic drug which reduces active sodium reabsorption and peripheral vascular resistance [6]. It treats fluid retention in congestive heart failure, cirrhosis of the liver, or kidney disorders, and may also be used to treat high blood pressure.

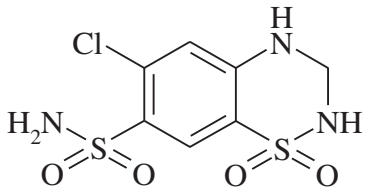
Several methods have been proposed for the individual or simultaneous determination of hydrochlorothiazide with other pharmaceutical compounds including chemometry [7], spectroscopy [8–11], capillary electrophoresis [12,13], high performance liquid chromatography (HPLC) [14–17], time resolved chemiluminescence [18], liquid chromatography/tandem mass spectrometry [19,20], chemometry [21], and electrochemistry [22–26].

In the past decades, there have been considerable attentions to the synthesis of metal nanostructures due to their different physical and chemical properties related to their similar large-scale ones, and potential applications in optical, electronic, catalytic and magnetic devices [27–29]. Among the metal nanostructures, nickel nanostructures have attracted much attention due to their applications in fabrication of sensors, biosensors, catalysts and conducting and magnetic materials [30–37].

In the present study, nickel nanowrinkles were synthesized through one-pot hydrothermal synthesis in the presence of fluoride ions. The nanowrinkles were then characterized and applied to modify carbon paste electrodes for the electrocatalytic oxidation and sensitive

* Corresponding author.
** Correspondence to: N. Sattarahmady, Department of Medical Physics, School of Medicine, Shiraz University of Medical Sciences, Shiraz, Iran.
E-mail addresses: hheli7@yahoo.com, heli@sums.ac.ir (H. Heli), nsattar@sums.ac.ir, sattarahmady@yahoo.com (N. Sattarahmady).

http://dx.doi.org/10.1016/j.microc.2016.09.005
0026-265X/



Scheme 1. Chemical structure of hydrochlorothiazide.

determination of hydrochlorothiazide. The nanowrinkles-modified electrode was then applied for quantitation of hydrochlorothiazide in bulk form, spiked human blood serum and tablets.

2. Experimental section

2.1. Materials

Graphite fine powder extra pure with a particle size of <50 μm was obtained from Merck (Catalogue Number 1042062500). Hydrochlorothiazide (>99%) was received from Darou Pakhsh Pharmaceutical Inc., Tehran, Iran. The hydrochlorothiazide tablets were purchased from a local drugstore. All other chemicals used in the experiments were of analytical grade from Merck or Sigma and used without further purification. All solutions were prepared with the doubly distilled water.

2.2. Synthesis of nickel nanowrinkles

Nickel nanowrinkles were synthesized by a simple, one-pot, hydrothermal method. In a typical procedure, 0.50 g $Ni(NO_3)_2 \cdot 6H_2O$ and 0.15 g NaF were firstly dissolved in 56 mL ethylene glycol. The obtained blue solution was transferred into a Teflon-lined autoclave of 80 mL capacity with a stainless steel shell, followed by hydrothermal treatment at 190 °C for 50 h. Then, the autoclave was allowed to reach the room temperature. The final product of the reaction as a black precipitate was filtered and washed several times with distilled water and then dried at ambient temperature.

2.3. Working electrodes preparation

Unmodified carbon paste electrode (UCPE) was prepared by careful hand-mixing graphite fine powder and mineral oil with a ratio of 80/20% (w/w). The paste was packed firmly into a cavity (2.2 mm diameter) at the end of a Teflon tube. Electrical contact was established by a copper wire.

Modified carbon paste electrodes with nickel nanowrinkles were prepared with different ratios of the modifier. Based on the results, the optimum modified electrode (NCPE) was obtained by mixing graphite fine powder, mineral oil, and nickel nanowrinkles with weight ratios of 75:20:5 for about 10 min. To cover the NCPE surface with a Nafion layer and provide the selectivity of the electrode, 10 μL of a

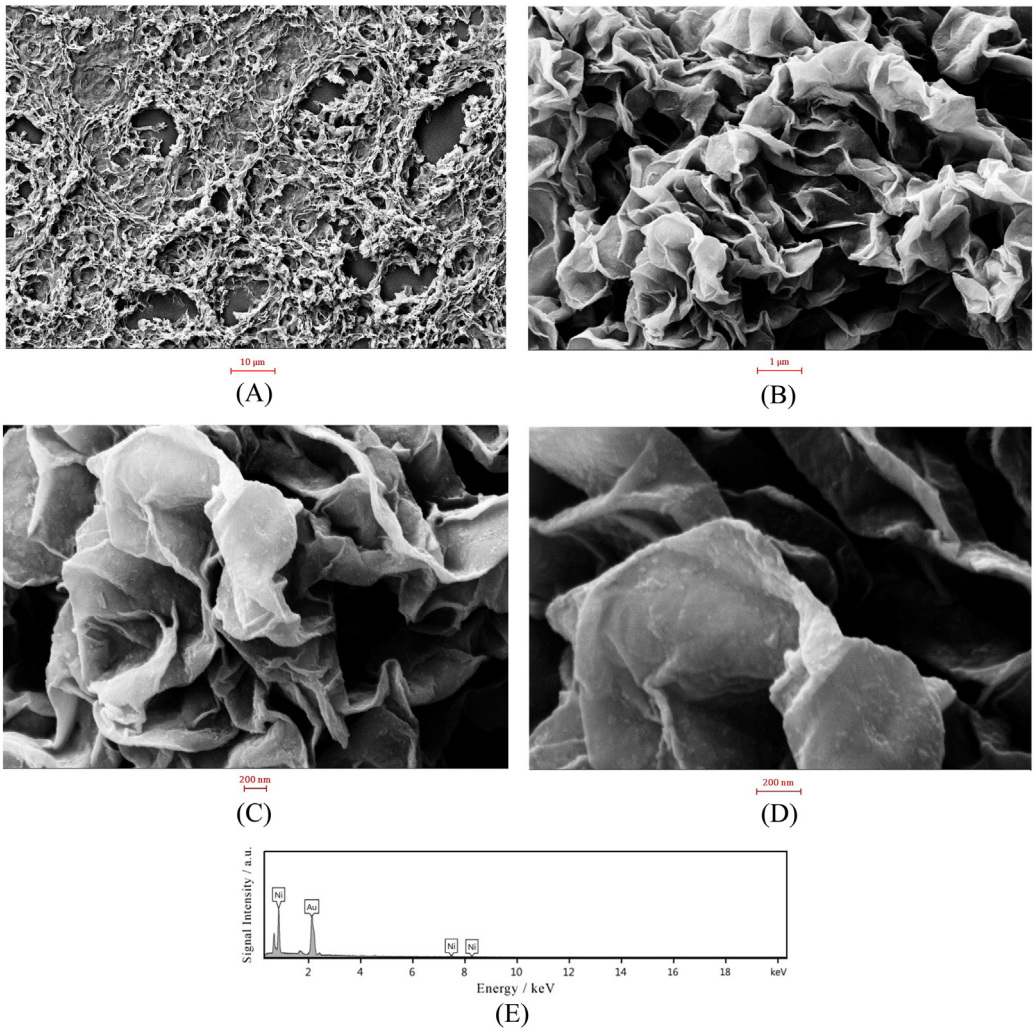


Fig. 1. SEM images (A–D) of nickel nanowrinkles with different magnifications, and an EDS spectrum (E).