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Detection Of Copper(II) Using a Nanostructured Modified Electrode in Biological Samples

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ABSTRACT

Identification of heavy metal ions has become a global problem due to continuous industrial and human pollution. In the present study, first, the synthesis of aluminate nanostructures was done by sol-gel method. Then, in order to study and measure copper(II) ions, a modified electrochemical sensor was designed based on synthetic nanostructures. Characterization of the nanostructures and designed nanostructure sensors was performed by various techniques including Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FE-SEM), electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV). The conducted studies showed the catalytic effect of the nanostructures for copper(II) ions. Then, the measurement of the analyte was investigated on the surface of a carbon paste electrode modified with the nanostructures. For this purpose, electrochemical techniques were studied. Then, the detection limit and dynamic linear range of copper(II) ions were determined by DPV technique. Therefore, the dynamic range of the analyte was from 0.02 µM to 350.00 µM and the detection limit was found to be 1.20 nM. Finally, for investigation of the ability of the proposed method, the analyte was detected in real samples and so that acceptable recovery percentages were obtained.

INTRODUCTION

The production of species that contain active oxygen as well as the cycle of oxidation and reduction is a reason for the chronic toxicity of copper in humans, which causes damage to the DNA part of the body. Acute copper poisoning usually does not occur due to the body's absorption and excretion regulation system. In case of very dangerous exposure to this metal, irreparable damages are caused to the kidneys and liver. Mammals have very efficient mechanisms to regulate copper reserves in a way that protects them from excess levels of copper in the diet [1-3]. Electrochemical techniques, especially voltammetry, are very sensitive techniques and due to its properties, they are promising methods for detecting heavy metal ions [4,5].

Nanotechnology is the ability to produce tools, materials and systems that can be achieved by controlling the level of molecules and atoms in nano dimensions. Nanostructures have gained an important position in the field of research due to having extraordinary effects such as electrical, optical, catalytic, medical, magnetic, and etc. properties [6-8]. In general, the smaller the size of materials and particles, the more amazing their properties are, and as a result, it causes changes in quantum effects and chemical reactivity [9]. In general, in the synthesis process of nanostructures, factors such as shape, size, and uniformity are very influential and important in their properties. They are classified from top to bottom [10-12]. One of the methods in the synthesis of the nanostructures is synthesis by natural materials. In this method, nanostructures are synthesized through plant extracts, agricultural waste and enzymes. Preparation of plant extracts is cheap and available in abundance. The synthesis in this way can be called the synthesis of nanostructures by the green chemistry method. So that, the synthesis of the nanostructures with this method reduces or prevents the use of dangerous and toxic substances, which is a factor in jeopardizing human health and the environment, and also reduces energy consumption. The synthesis of the nanostructures with the help of plant extracts is economically very economical and thus it can be used as an alternative and valuable method for the production of

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nanostructures [13]. Plant extracts include alkaloids, biomolecules, enzymes, proteins, amino acids, phenolic compounds, alcohol, polysaccharides, etc., which are used to reduce, stabilize and cover nanoparticles. [14,15].

The sol-gel method is one of the bottom-up synthesis methods, which is used to produce homogeneous metal oxides with high purity of ceramic particles. This method is one of the common methods in the production of nanostructures in the liquid phase due to the ease and diversity of the formed products and the need for no special equipment [16]. The advantages of the soll-gel method include low cost, production of high purity products, no need for expensive equipment, ease of reaction, possibility of synthesis at low temperature, increase of chemical reactivity in precursors. The reason for the production process in the solution phase is the increase in product quality, the application of the method in the industry, the uniformity of the produced products, the possibility of preparing coatings and fibers in a wide range of solid materials, facilitating the synthesis of porous materials [17,18]. Also, in the sol-gel combustion method, metal salts, which are mostly nitrates, act as oxidants, and organic compounds act as fuels and reducers [19].

Sodium aluminate is a kind of strong base that is insoluble in alcohol and soluble in water [20]. Thus, it has many uses as electrocatalyst, catalyst, and etc. Also, sodium aluminate has the ability to catalyze transesterification to produce biodiesel. therefore, its interaction with the hydrogen present in alcohol is easily done so that the solution becomes strongly alkaline [21]. Unfortunately, the corrosiveness and moisture of sodium aluminate leads to the inactivation of the catalyst and the reduction of the life of the equipment, which is against its direct use in esterification. In addition, aggregation to form large particles leads to low efficiency of the catalyst. Therefore, it is expected that sodium aluminate will be dispersed in nano sizes and placed on bases with a strong and high surface. Hence, the reactive molecules can reach the surface active sites, so the nanostructures can be used as potential materials for catalytic applications [22].

In the past, a series of metallic electrodes such as mercury, platinum, silver or conductive non-metallic electrodes such as graphite have been used for electrochemical processes. Apart from mercury, the disadvantages of these electrodes include low selectivity, lack of reproducibility of the behavior of the electrode surface, strong absorption and also sometimes the irreversibility of the desired species on the electrode surface, as well as changing the characteristics pointed electrode surface. Chemically modified electrodes (CMEs) have been created to solve this problem. In this way, there are many advantages for such electrodes such as high selectivity, improvement in sensitivity, low overvoltage, protection against unwanted reactions from the electrode surface and increasing the stability of the electrode. If the surface of the electrodes is modified, the electrode systems will advance in many fields such as highly sensitive biological measurements, protection against corrosion and electrosynthesis. Among the most important methods that are used to modify the electrodes, one can use the modified electrodes based on surface absorption, by creating a covalent bond, based on the property of dissolution in lipophilic substances, directly combining the modifier composition and positioning with selectable coatings [23-25].

One of the objectives of the present study, is to measure pollutant materials in real samples. Among these pollutants copper(II) ions were selected. So far, a variety of methods have been used to remove heavy metals, including filtration methods, chromatography, spectroscopy, and etc. But in the meantime, electrochemical methods have been of interest due to their unique characteristics, including sensitivity, high speed, ease of operation, cost-effectiveness, and high selectivity. Therefore, in the present research, the electrodes were modified with aluminate nanostructures and have been used as high sensitive sensor for trace analysis of copper(II) ions in biological samples, and acceptable results have been obtained.

MATERIALS AND METHODS

Chemicals

Sodium hydroxide, phosphoric acid, boric acid, acetic acid and other chemicals were from Merck with analytical grade and used without any other purification. Deionized water was used in all stages of the experiment. In the studies related to copper(II) ions, Britton-Robinson (B-R) buffer with a concentration of 0.2 M was used. To prepare the buffers with desired pH, first a 0.2 M solution containing three acids (H_3PO_4, CH_3COOH, and H_3BO_3) was prepared and then the buffer was adjusted with a saturated sodium hydroxide solution using a pH meter. The modified electrodes include graphite powder, paraffin oil ($\rho = 0.88$ g cm^{-3}), and optimal amounts of the aluminate nanostructures. Meanwhile, a polyethylene tube with an opening diameter of 2 mm and a length of 5 mm was used as a holder, so that the electrodes were connected to the device through a wire.

Apparatus

The study of nanostructures was done by Shimadzu Varian 4300 Fourier transform infrared spectrophotometer (FT-IR) in KBr. Field emission scanning electron microscopy (FE-SEM) was recorded with XL-30ESEM device. Electrochemical impedance spectroscopy (EIS) was performed on a PGSTAT 35 potentiostat-galvanostat (Eco chemie Utrecht, Netherlands). The test conditions were controlled by Nova 1.6 Autolab software. Other electrochemical experiments were performed by SAMA 500 potentiostat (SAMA Research Center, Iran) using a typical three-electrode system including a platinum electrode (Azer Electrode-Iran) as an contour electrode, Ag/AgCl, KCl 3.0 M (Azer Electrode-Iran) as a reference electrode, and a modified or bare carbon paste electrode as a working electrode. An ATRON model pH meter (Metrohm, Switzerland) was used to adjust the pH of the solution. An ultrasonic bath, ULTRASONIC CLEANER (Ps-10A, China) was used to disintegrate of the nanostructures. A digital analytical balance model R 160 p, Sibgene, Germany was used for the experiment. Also,

MEMMERT UE (Germany) oven and Naberthem L3 electric furnace (Germany) were used for temperature regulation and calcination steps.

Synthesis of the nanostructures

An appropriate of $Al(NO_3)_3.9H_2O$ was weighed and dissolved in 10 mL of deionized water. Also, a stoichiometric amount of sodium sulfate salt (Na_2SO_4) was dissolved in 10 mL of deionized water and these two solutions were added to 10 mL of sour tea extract. Then, the pH of the solution was adjusted between 10-12 by ethylenediamine [26]. The resulting solution was kept at a temperature of 50ºC for 3 h, and after the water evaporated and turned into a gel-like state, it was placed in an oven at a temperature of 100ºC for 24 h. Then, the resulting composition was transferred to the furnace for calcination under the temperature conditions of 900 ºC and a duration of 3 h (optimal conditions).

Preparation of the modified electrode

In order to make the modified electrode, a specific amount of the synthesized nanostructure was first weighed and then 10 mL of deionized water was added and the resulting mixture was homogenized using an ultrasonic bath. Then, a certain amount of graphite powder was added to the obtained composition and its drying process was carried out at 60 ºC. Next, 0.18 g of paraffin oil was added to it and after mixing them completely to make a homogeneous paste, the created paste was transferred into a polyethylene tube.

Preparation of the real samples

In the present research, biological real samples were used to measure the copper(II) ions To prepare the hair samples, the following procedure was as. First, the hair samples were weighed and then washed twice with distilled water and dried under the temperature conditions of 110ºC for 2 h. Digestion was done in a period of 4 min and at a temperature of 44ºC by adding 4 mL of concentrated sulfuric acid and finally 10 mL of hydrogen peroxide was added to the resulting mixture. After a short period of time, when the solution becomes white and transparent, the solution was cooled and brought to a volume of 50 mL, and used for measurement [27].

RESULTS AND DISCUSSIONS

Characterization of the nanostructures

Fourier transform infrared spectroscopy was used to investigate and identify functional groups. Fig. 1 shows the FT-IR spectrum of sodium aluminate nanostructures. In this spectrum, the absorption peak at 3444 cm^{-1} indicates the stretching vibrations of the O-H group. Also, the absorption bands at 1636 cm^{-1} and 1382 cm^{-1} are attributed to the bending vibrations of water molecules. The main absorption peaks in the region of 620 cm^{-1} and 554 cm^{-1} can be related to metal-oxygen stretching vibrations. Thus, by the results, it can be concluded that there are no impurities on the surface of sodium aluminate nanostructures [28,29].

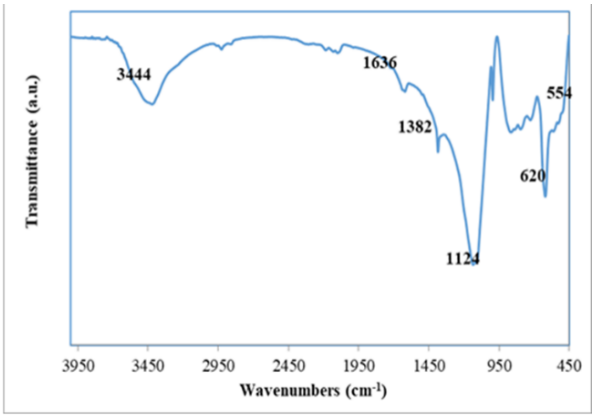


Fig. 1. FT-IR spectrum of aluminate nanostructures.

FE-SEM method was used to confirm the formation, morphology and particle size of the aluminate nanostructures. The FE-SEM micrograph of the nanostructures is shown in Fig. 2. Based on this figure, the morphology of spherical to cylindrical particles can be observed and the size of synthetic nanostructures is in the range of 40-50 nm.

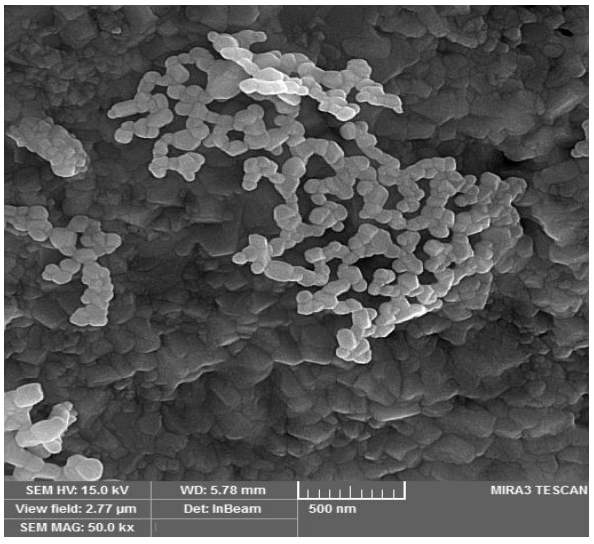


Fig. 2. FE-SEM micrograph of aluminate nanostructures.

FESEM studies of the modified electrode

In order to study the modified nanostructured carbon paste electrode with sodium aluminate nanostructures ($NaAlO_2$/CPE), FE-SEM micrographs have been used. Fig. 3 (a) shows the micrograph of the unmodified carbon paste electrode. Also, Fig. 3 (b) presents the micrograph of the $NaAlO_2$/CPE. According the studies in Fig. 3 (a) the carbon paste electrode contains graphite powder with non-uniform plates. However, Fig. 3 (b) shows by the modification of the electrode surface, the process of placing sodium aluminate nanostructures on graphite plates becomes possible.

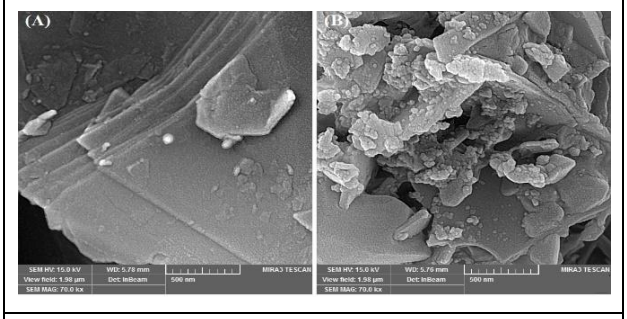


Fig. 3. FE-SEM micrographs at the surface of (A) unmodified carbon paste electrode and (B) $NaAlO_2$/CPE.

Characterization of the nanostructured modified electrode by EIS

EIS is a useful techniques to study and identify the surface characteristics of modified nanostructured electrodes. Fig. 4. shows the Nyquist diagram of the unmodified and modified electrode with sodium aluminate nanoparticles in the presence of 5.0 mM iron II and III probe solution in 0.2 M B-R buffer with pH=7.00. According to Fig. 4(a), there is an obvious difference between the charge transfer resistances (R_{CT}) of the two electrodes. Thus, the R_{CT} for the unmodified carbon paste electrode was 1.21 KΩ and for $NaAlO_2$/CPE is obtained 0.21 KΩ. This reduction in R_{CT} can be attributed to the facilitation of electron transfer by sodium aluminate nanostructures on the surface of the modified carbon paste electrode.

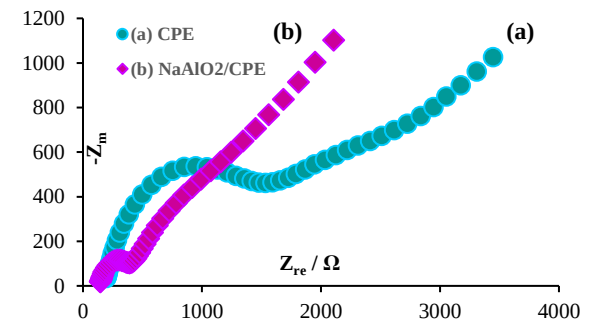


Fig. 4. Nyquist curve of (a) unmodified carbon paste electrode and (b) $NaAlO_2$/CPE in the presence of 5.00 mM of $[Fe(CN)_6]^{3-/4-}$.

CV analysis of the nanostructured modified electrode

In order to more study of the electrochemical behavior of the nanostructured modified carbon paste electrode, cyclic voltammograms of a solution containing 5.00 mM of $[Fe(CN)6]^{3-/4-}$ probe at pH=7.00 have been investigated. Fig. 5 shows that the cyclic voltammogram of the probe solution at the surface of the nanostructured modified electrode has increased by about 3.5 times and the corresponding peak potential has decreased by 62 mV compared to the unmodified electrode. The results clearly show the presence of the nanostructures at the surface of the modified electrode and their effect in increasing sensitivity and reducing overvoltage. In fact, it shows the catalytic character of the nanostructures. Therefore, it can be concluded that sodium aluminate nanostructures facilitate the process of electron transfer to the electrode surface.

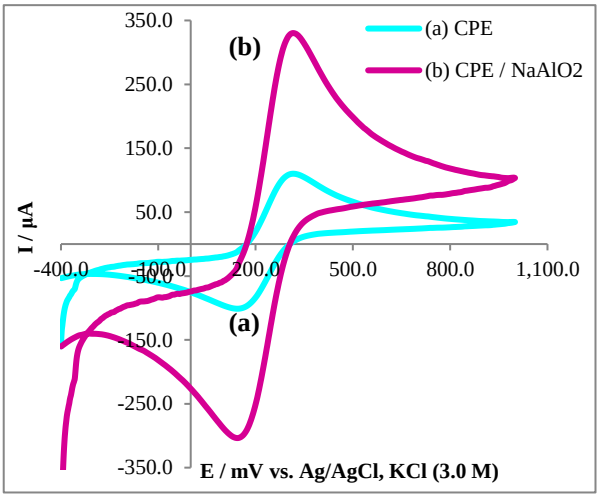


Fig. 5. Cyclic voltammograms of (a) unmodified carbon paste electrode and (b) $NaAlO_2$/CPE in the presence of 5.00 mM $[Fe(CN)_6]^{3-/4-}$.

Electrochemical behavior of Cu(II) at the surface of the nanostructured electrode

In order to achieve the catalytic activity of NaAlO2/CPE for analysis of Cu(II), differential pulse voltammetric responses in the presence of 50.00 µM copper(II) in B-R buffer 0.2 M (pH=4.88) were investigated. Fig. 6 shows differential pulse voltammograms of copper heavy metal at the surface of unmodified and modified nanostructured electrodes. It can be observed at the surface of the modified electrode the oxidation peak current of Cu(II) ions is enhancement more than three times than the unmodified carbon paste electrode. The results indicate the high sensitivity of the nanostructured electrode for analyzing of the analyte.

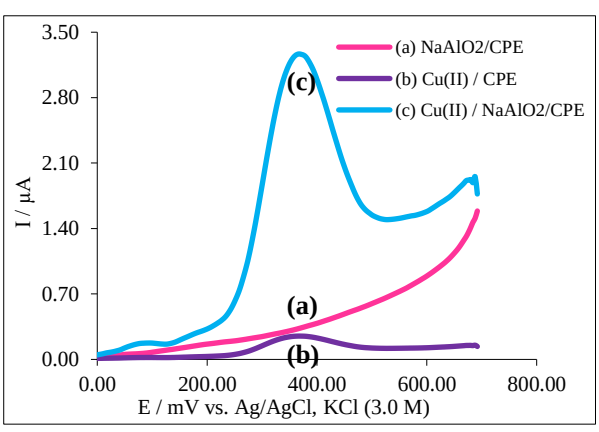


Fig. 6. Differential pulse voltammograms of B-R buffer (pH=4.88) at the surface of (a) unmodified carbon paste electrode in the presence of 50.00 µM of copper (II) ion, (b) $NaAlO_2$/CPE, and (c) NaAlO2/CPE in the presence of copper (II) ions.

Calibration curve and limit of detection of Cu(II)

Differential pulse voltammetry (DPV) techniques was used to measure the detection limit of copper(II) ions. Fig. 7 (A) shows differential pulse voltammograms of different concentration values of copper(II) ions under the optimal conditions. Also, the oxidation peak currents of the analyte in different concentrations were measured and calibration curve was plotted (Fig. 7 (B)). Using the study two broad dynamic ranges were obtained containing 0.02-0.80 µM and 0.08-350.00 µM. Then, for determination the detection limit of copper(II) ions at the surface of $NaAlO_2$/CPE, the differential pulse voltammograms of B-R buffer were recorded and the detection limit was obtained 1.20 nM. In Table 1, some of the analytical parameters of the present study were compared with previously works [30-35]. These data indicate that the responses of the proposed sensor are superior to the previously reported methods.

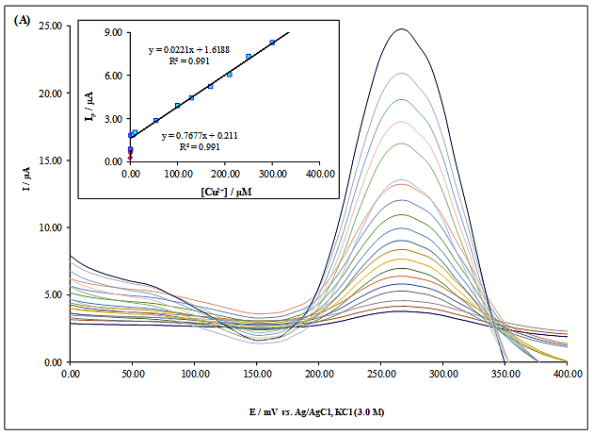


Fig. 7. (A) Differential pulse voltammograms of $NaAlO_2$/CPE in B-R buffer at different concentration values of copper(II) ions and (B) The corresponding calibration curve.

Table 1
Comparison of analytical parameters of several Techniques for Cu(II) ions determination.

Technique	Detection limit (nM)	Linear range (µM)	Reference
Cyclic voltammetry	260.00	1.96-5.66	30
Differential pulse anodic stripping voltammetry	251.77	20.00-950.00	31
Square-wave anodic stripping voltammetry	23.92	0.002-0.79	32
Square-wave voltammetry	10.00	1.23-400.00	33
Square wave voltammetry	5.00	0.0075-0.18	34
Square wave anodic stripping voltammetry	1.73	0.16-1.10	35
Differential pulse voltammetry	1.2	0.02-350.00	This work

Real Sample Analysis

In order to investigation of the ability of the proposed method for detection of Cu(II) ions in real samples, biological samples such as human hair were studied. For achieving the purpose DPV technique and standard addition methods were used. The results obtained from the standard addition method in different samples are shown in Table 2. According to the obtained results, the percentages of addition recovery in the considered samples are acceptable, which indicates the ability of the proposed method to detect Cu(II) ions in biological samples.

Table 2
Standard addition method for detection of Cu(II) ions in human hair samples.

Sample of human hair	Added (µM)	Found (µM)	Recovery (%)
1	0.0	3.3	_
2	5.0	8.0	96.3±1.2
3	10.0	13.5	101.2±0.9
4	15.0	18.5	101.0±1.7
5	20.0	22.8	97.3±1.1
6	25.0	27.6	97.1±0.8

CONCLUSIONS

In this study, aluminate nanostructures were first synthesized and identified. Then, using the nanostructures, a new electrochemical sensor was designed and identified in order to study and analysis of the heavy metal copper in complex real samples. Measurements and investigation of copper species at the surface of the nanostructured modified electrode was performed using electrochemical methods. The dynamic linear range and detection limit of copper(II) ions were calculated. The results showed that the measurement of copper ion by the proposed nanostructure electrode is possible with a wide linear range, high sensitivity and without any interferences. In addition, the measurements for copper(II) ions at the surface of $NaAlO_2$/CPE were performed in biological real samples. According to the observed results, detection of copper(II) ions in the real samples were performed with acceptable results. Therefore, the proposed nanostructured electrode can be a good candidate for sensitive detection of pollutants in real complicated samples.

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