Electrochemical sensitivity, selectivity, and sensory properties of a natural polymer-supported titanium nanocomposite electrode towards lysine amino acid

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ABSTRACT

In this study, chitosan (Chit) supported titanium (Ti) nanoparticles (Ti@Chit NPs) were synthesized by chemical method. Ti@Chit NPs were calculated to be 7.275 ± 2.15 nm and 18.629 nm according to scanning electron microscopy (SEM) and atomic force microscopy (AFM) results, respectively. The synthesized NPs were modified to the electrode and a sensitivity study was carried out against lysine amino acid. It has been determined that the Ti@Chit electrode has a catalytic performance against the amino acid lysine. The limit of detection (LOD) value is estimated to average 0.0041 µM.

Keywords: Lysine, Sensor, Ti@Chit NPs

Doğal polimer destekli bir titanyum nanokompozit elektrodun lizin amino aside karşı elektrokimyasal duyarlılığı, seçiciliği ve duyusal özellikleri

ÖZ

Bu çalışmada kitosan (Chit) destekli titanyum (Ti) nanoparçacıkları (Ti@Chit NPs) kimyasal yöntemle sentezlendi. Ti@Chit NP'leri taramalı elektron mikroskobu (SEM) ve atomik kuvvet mikroskobu (AFM) sonuçlarına göre sırasıyla 7,275 ± 2,15 nm ve 18,629 nm olarak hesaplanmıştır. Sentezlenen NP'ler elektroda modifiye edildi ve lizin amino aside karşı bir duyarlılık çalışması yapıldı. Ti@Chit elektrodunun amino asit lizine karşı katalitik bir performansa sahip olduğu belirlenmiştir. Tespit sınırı (LOD) değerinin ortalama 0,0041 µM olduğu tahmin edilmektedir.

Anahtar Kelimeler: Lizin, Sensör, Ti@Chit NPs

INTRODUCTION

Amino acids are the smallest building blocks of proteins, which are vital for living metabolism [3]. Therefore, applications for the diagnosis of amino acids are important for researchers [2-4]. In particular, lysine is the most rapidly damaged and degraded amino acid type [5],[6]. The durability of lysine plays a very important role due to its applications such as the use of lysine in food supplements, the use of diet therapy. For this reason, researchers have turned to sensor applications for the diagnosis of lysine [7-9]. According to a study in the literature, sensor studies were carried out with lysine carbon nanotube supported composites [10]. In another previously reported study, electrodeposited applications for lysine were performed [11]. Sensors play an important role in the diagnosis of lysine and amino acids.

Sensors are systems that convert chemical data into specific signals [12], [13]. The mechanism of the sensors is based on the fact that they produce continuous signals depending on the concentration for better examination of the structure of an analyte [14]. The fact that the sensors are fast, practical, cheap and economical provides great advantages in applications. For example, chitosan polymer was reduced to nano size and supported lead sensor application was carried out on the shicff base [15]. Nowadays, virus sensors have been developed by supporting the sensors with chips in technological studies [16]. Nanotechnological studies occupy an important place in sensor applications. Nanotechnology is a science that deals with the nano size between 1-100 nm [17]. Especially nano metals are used as catalysts in catalytic reactions. Platinum is a highly preferred metal in nanotechnological studies [18], [19]. Apart from this, metals such as silver [20], gold [21], iron [22], nickel [23], cobalt [24] etc are also used in nanotechnological studies. Support materials are used to improve the catalytic performance of nanometals. In addition to chemical support materials, polymeric materials obtained from natural sources are preferred in terms of being environmentally friendly, non-toxic, and easy to apply.

In sensor applications, supporting materials such as multi-walled carbon nanotubes, graphene oxide or activated carbon are used to improve the performance of nanometals [25]. These support materials help increase the conductivity of electrons by expanding the surface

area [26]. Biocompatibility of nanoparticles with chitosan, non-toxic properties, cost effectiveness and high permeability have gained great importance. For this reason, nanometals are used together with chitosan [27]. The use of nanoparticles in the identification of proteins such as lysine covers a wide area. Since the use of nanoparticles with chitosan will increase stability, the use of polymers such as lysine in the sensor is among the subjects of the researchers [28]. In some studies, research has focused on natural polymers by researching the use of support materials with non-toxic agents [15]. Chitosan is one of the natural polymers [29]. Chitosan is obtained by deacetylation method from the chitin layer found in the shells of insects, shrimps, lobsters and crabs [30]. Commercial forms are available in nature according to the degree of deacetylation [31], [32].
In this article, nano-sized chitosan-based titanium particles were obtained by a series of processes by supporting titanium metal with chitosan polymer. A voltammetric sensor for lysine amino acid was developed with the obtained. Ti@Chit NPs were supported by AFM and SEM.

MATERIAL and METHOD

Materials

Titanium dioxide, chitosan, acetic acid, NaOH, ethanol and all chemicals were supplied by Sigma & Aldrich. Chitosan has a 90% degree of acetylation.

Preparation of Ti@Chit NPs

60 ml are separated, and 1 g of chitosan is added to the mixture after the acetic acid has been adjusted to 0.5% by volume. 120 cc of titanium dioxide were then added along with 12.8 mmol/L. The response happened a day later. The precipitates were then filtered, dried, and kept for sensor experiments after the pH level was brought down to 8 with 0.1 M sodium hydroxide [33].

RESULTS and DISCUSSION

Characterizations

SEM and AFM characterization devices used to determine the surface size of nanoparticles and to observe the structure of their shape are ZEISS EVO LS10 and NT-MDT / Ntegra Solaris model devices, respectively. Voltammetric measurements were performed on a Gamry Potentiostat/Galvanostat 400 brand device.

SEM analysis

In figure 1, SEM characterization graph of lysine amino acid and chitosan-supported titanium nanoparticles on lysine is given. As seen in figure 1, it is observed that the amino acid lysine is spherical and has a sharp structure [34]–[37]. On the other hand, the titanium nanoparticles seen in figure 2 entered the lysine cavities and filled them by clustering (a), and the particle size is estimated to be 7.275 ± 2.15 nm on average (b) [38]. The results are consistent with the studies in the literature [31], [32].

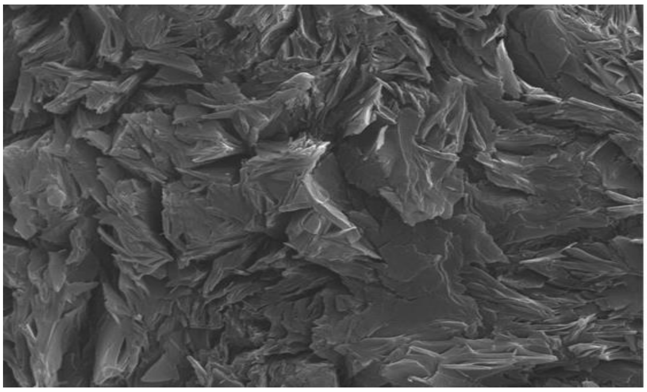

Figure 1. SEM characterization of lysine amino acid

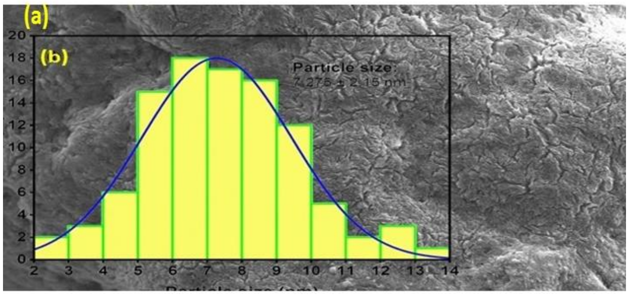

Figure 2. Figure 2. SEM characterization of (a) Ti@Chit NPs on lysine (b) the histogram of NPs

AFM analysis

In figure 3, AFM analysis is given to observe the position and nano size of Ti@Chit NPs hidden between the lysine amino acid. According to figure 3, the nanoparticles clustered and agglomerated in some places and showed a monodisperse distribution in some places. The 3-dimensional height and topographic distribution of the nanoparticles are given in figure 4. It was determined that the nanoparticles were 18.629 nm on average [39].

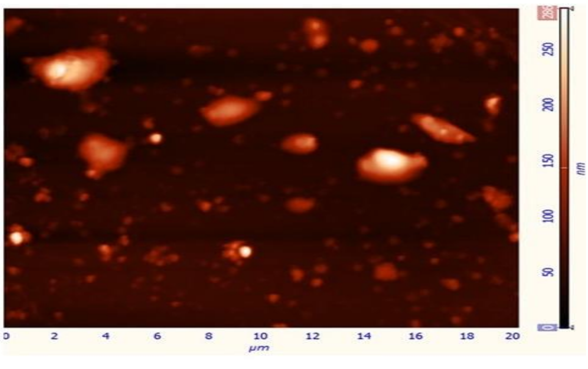

Figure 3. AFM analysis of Ti@Chit NPs as 2D (B) 3 D dimension of NPs

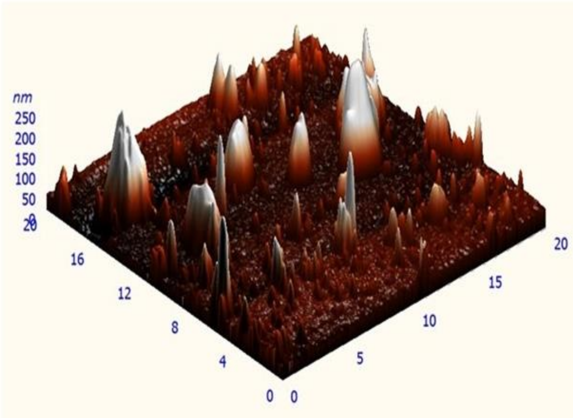

Figure 4. AFM analysis of 3 D dimension of NPs

Voltammetric studies

The rate scan (0.1-0.4 V/s) of Ti@Chit nanoparticles for lysine amino acid is as in figure 5. According to Figure 5, it is seen that the amount of current increases as the scan rate increases. On the other hand, potential ranges against currents of CV analysis are observed and the highest peak is observed in the range of 0.68-0.69 µM according to figure 6.

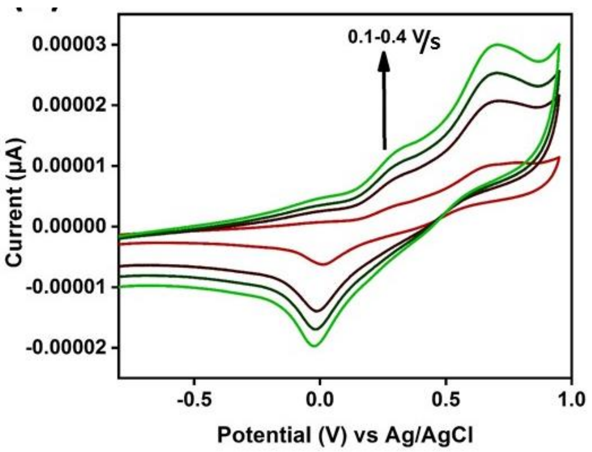

Figure 5. Cyclic voltammogram of Ti@Chit NPs against lysine

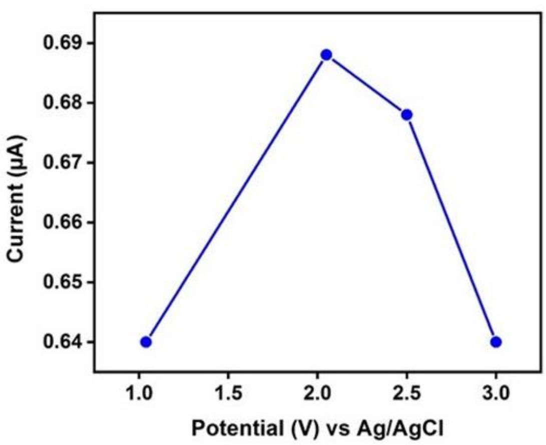

Figure 6. Current peaks againt voltage potentials

According to figure 7, the sensitivity of the modified Ti@Chit electrode, modified Ti electrode and modified chitosan electrode to lysine is shown. According to figure 8, the selectivity of the peaks where the electrodes show the highest sensitivity is shown. According to figure 9, the linear graphic curve of the current values is shown. The LOD value is estimated to be 0.0041 µm.

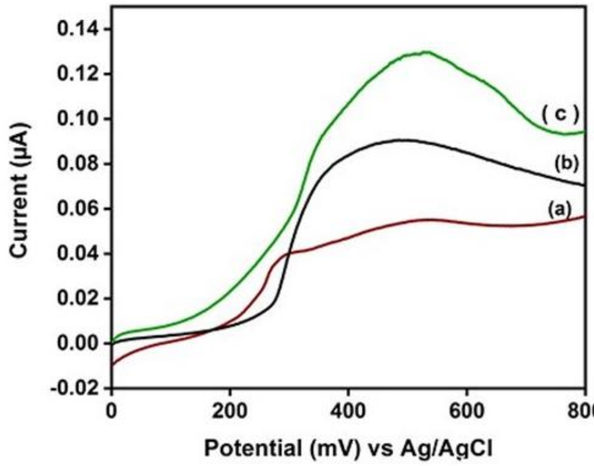

Figure 7. Selectivity of electrodes against lysine (a) Ti@Chit (b) Chit (c) Ti@Chit

This study showed a very good sensor property by showing sensitivity at the micromolar level compared to previous studies.

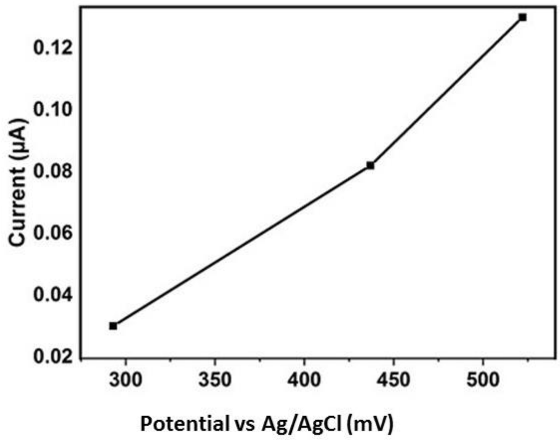

Figure 8. The peaks of highest current values

Table 1. Sensitivity of electrodes to lysine in previous studies and the value of this study

Electrodes	LOD values	Ref
(AuNPs)/poly(L-lysine) complex	3.5×10^{-14} M	[40]
$PVF^{+}LyOx^{-}/Pt$	6.5×10^{-4} mM	[11]
GOx	2.0 mM	[41]
Ti@Chit	0.68-0.69 µM	This study

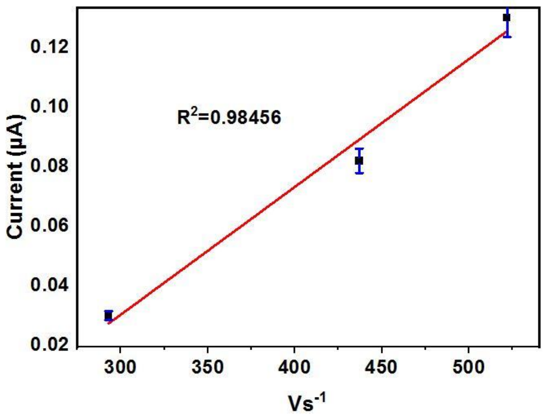

Figure 9. Lineer graph error bars values

CONCLUSION

Using chemical method, Ti@Chit NPs were synthesized and their sensitivity to lysine amino acid was measured. The synthesized nanoparticles were first subjected to SEM and AFM characterization analyses. It was determined to be 7.275 ± 2.15 nm according to SEM analysis and 18.629 nm according to AFM analysis. At the same time, it was observed in the SEM analysis that the amino acid had a sharp structure and the nanoparticles were in between the amino acids. According to the AFM analysis, the nanoparticles were partially agglomerated and in some places did not agglomerate. In voltammetric studies, it was observed that the current intensity of the Ti@Chit electrode against amino acid increased with the increase in scanning speed. According to the comparison of the electrodes, it was determined that Ti@Chitamino acid showed the highest catalytic result against lysine. The average LOD value in this study is estimated to be 0.0041 µM.

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