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Application of polyoxometalate/carbon nitride nanotubes nanocomposite for directly methanol oxidation

Doğrudan metil alkol oksidasyonu için polioksometalat/karbon nitrit nanotüp nanokompozitinin uygulanması

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Abstract

Fuel cell in this study consumes methanol as fuel and they are very important for clean environment and effective energy conversion. Graphitic carbon nitride (g-C_3N_4) is carbon allotrope among carbon based nanomaterials. It consists of C–N bonds in π-based polymer. Polyoxometalates (POMs) are redox-active materials and have crucial potential for direct methanol oxidation and energy storage. POMs attract important interest because they included in high-valent metals and anionic metal oxides. In present report, the nanocomposite of polyoxometalate/C_3N_4 NTs was synthesized and applied for fuel cell. Firstly, the structure of prepared nanocomposite was investigated by transmission electron microscope (TEM), x-ray photo electron spectroscopy (XPS) and scanning electron microscope (SEM). After that, the voltammetric measurements were performed by using nanocomposite modified electrode. The electrochemical active areas of POM-C_3N_4 NTs/GCE and C_3N_4 NTs/GCE are 0.511 cm^2 and 0.169 cm^2, respectively. The prepared nanocomposite demonstrated active catalytic effect towards methanol.

Keywords: Nanokompozit, Karbon nitrit nanotüp, Polioksometalat, Doğrudan yakıt hücresi

Öz

Bu çalışmada geliştirilen yakıt hücresinde yakıt olarak metil alkol kullanılır. Methanol yakıt hücreleri özellikle temiz çevre ve etkili enerji dönüşümü için çok önemlidir. Grafit karbon nitrit (g-C_3N_4) karbon bazlı nanomateryaller arasında kararlı karbon allotropudur. Π bazlı polimer sisteminde elektron lokalizasyonu olmayan C – N bağlarından oluşur. Polioksometalatlar (POMs) redoks-aktif maddelerdir ve doğrudan metanol oksidasyonu ve enerji depolama için hayati bir potansiyele sahiptir. POM'lar, yüksek değerli metaller ve anyonik metal oksitler içerdikleri için ilgi görmektedir.Bu çalışmada, Polioksometalat/ karbon nitrit nanotüp (C_3N_4 NTs) sentezlenmiş ve yakıt hücresi için uygulanmıştır. Öncelikle, hazırlanan nanokompozitin yapısı geçirgen elektron mikroskopu (TEM), x-ışınları fotoelektron spektroskopisi (XPS) ve taramalı elektron mikroskopu (SEM) kullanılarak incelenmiştir. Daha sonra bu nanokompozit modifiyeli elektrot kullanılarak elektrokimyasal ölçümler gerçekleştirilmiştir. POM-C_3N_4 NTs/GCE ve C_3N_4 NTs/GCE elektrotların elektrokimyasal aktif yüzeyleri sırasıyla 0.511 cm^2 ve 0.169 cm^2 olarak bulunmuştur. Hazırlanan nankompozit metil alkole karşı aktif bir katalitik etki göstermiştir.

Anahtar kelimeler: Nanocomposite, Carbon nitride nanotubes, Polyoxometalates, Direct fuel cell

1 Introduction

Fuel cell, which occur through consuming of methanol-based fuels are 25% more than compared to other fuels. Some of the fuels used in energy cell becomes inert and harmless. However, most of them accumulated in different parts of environment like agriculture or water samples and poses serious environmental risks. In a fuel cell, it is possible to convert the energy of the fuel directly into the electrical energy. Their union is only carried out by ion and electron transfer between these compartments [1],[2].

The fuel cell converts the energy of fuel directly into electrical energy through the electrochemical reaction producing electricity with external fuel (anode side) and oxidizer (cathode side). They react in an electrolyte/electrode unit. Generally, when the reactants enter the cell, the reaction products leave from the cell. Fuel cells can work forever as long as the required fuel and oxidant flow is achieved. The methanol fuel cell is very important source for clean, effective and active energy. In addition, it is utilized as suitable power source. The methanol as fuel in fuel cell is liquid at room temperature. It has effective energy density and low cost. In the system of direct fuel cell, there are two electrode systems such as positive and a negative electrodes in contact with a film including in hydrogen or hydronium ion [3]-[5].

New materials that are formed by combining at least two different materials at the macro level are called composite materials. The purpose of the composite production is to add new features to make the materials giving the suitable properties to the usage areas. (Strength, lightness, flexibility, cost, etc.). g-C_3N_4 is carbon allotrope among carbon based nanomaterials. g-C_3N_4 has important energy applications such as fuel cell. In its structure, van der waals interactions are dominant. It is utilized for nanosensor and catalytic applications. Its tubular structure (C_3N_4 NTs) is able to improve the transfer of ion and diminish the transfer of mass owing to effective edges [6]-[9]. Polyoxometalates (POMs) are redox-active materials and have crucial potential for direct methanol oxidation and energy storage. POMs attract important interest because they included in high-valent metals and anionic metal oxides [10]-[13].

The target of this study is built up of a novel fuel cell, which is able to determine methanol effectively from supporting electrolyte via POM-C_3N_4 NTs/GCE. For this purpose, the nanocomposite modified electrodes were prepared and characterized.

2 Experimental procedure

2.1 Chemicals

The used agents in present work are H3PW12O40, melamine, methanol, acetonitrile, perchloric acid were obtained from Merck, Germany and Sigma-Aldrich.

2.2 Synthesis of nanomaterials

The utg-C_3N_4 and C_3N_4 NTs were obtained according to work [14]. For nanocomposite preparation of $H_3PW_{12}O_{40}$/C_3N_4 NTs; 0.20 g of POM was dissolved in grade acetonitrile. This solution added into 0.50 g of utg-C_3N_4. After 2 h, the hydrothermal treatment at 2000 ^oC applied to the solution. After drying at 50 ^oC, POM-C_3N_4 NTs was evaluated [15].

2.3 Procedure for the electrode preparation

Glassy carbon electrode (GCE) was prepared according to the reports [16],[17]. After that, the POM and POM-C_3N_4 NTs catalyts were prepared into 2.0 mL of ethanol. After that, the solvent was removed by IR.

2.4 Electrochemical measurements

In present study, the modified electrodes were utilized as working catalysts in fuel cell system. The fuel (methanol) was prepared in 0.1 mol L^{-1} perchloric acid. After the potential application to working electrode, the electrochemical data were obtained relating to methanol oxidation.

3 Results and discussions

3.1 Characterization of nanomaterials

Figure 1A shows the aggregated structure of g-C_3N_4. Ultra-thin g-C_3N_4 was generated under ultrasonication (Figure 1B). Tubular C_3N_4 NTs nanostructure was formed by hydrothermal treatment at 200 °C. Figure 1C verifies the tubular structure of C_3N_4 NTs. Figure 1D shows the TEM image of the nanoscale of the POM-C_3N_4 NTs. POM clouds on surfaces of C_3N_4 NTs were obtained. Therefore, it can be said that the interface interaction between POM and C_3N_4 NTs results in POM-C_3N_4 NTs formation.

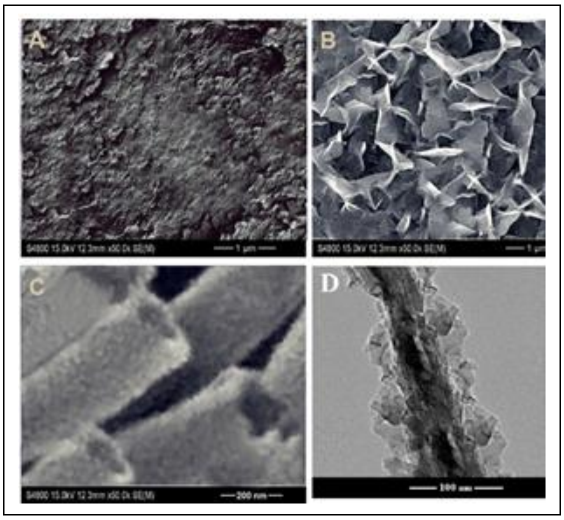

Figure 1: SEM images of prepared nanomaterials in present study.

XPS analysis confirms POM-C_3N_4 NTs presence (Figure 2). The peaks relating to C1s, N1s, P2s, W4f and O1s confirm the interfacial interaction between POM and C_3N_4 NTs materials.

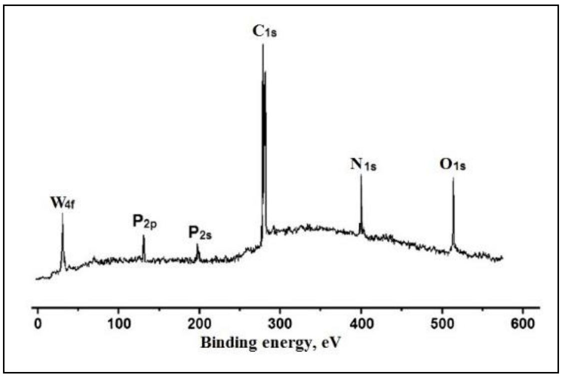

Figure 2: XPS image of POM-C_3N_4 NTs nanocomposite.

3.2 Electrochemical performances of modified electrodes

Firstly, the electroactive areas of C_3N_4 NTs/GCE and POM-C_3N_4 NTs/GCE was calculated by cyclic voltammetry by "$ip=2.69\times10^5\ A\ n^{3/2}\ D^{1/2}\ C\ v^{1/2}$" where ip is the signal, C is the concentration of $[Fe(CN)_6]^{3-}$, v is the scan rate and A is the surface area (cm^2). The electrochemical active areas of POM-C_3N_4 NTs/GCE and C_3N_4 NTs/GCE are 0.511 and 0.169 cm^2, respectively. The electrocatalytic activities towards 0.5 M methanol in perchloric acid were explained by using prepared electrodes in this work. The current peaks were evaluated during forward and reverse scans (Table 1). The I_f of POM-C_3N_4 NTs/GCE was 3.67 times higher than that of C_3N_4 NTs/GCE, respectively (Table 1).

Table 1: Comparison of modified electrodes against methanol oxidation.

Electrode	If (A cm^{-2})	E (V)	Ib (A cm^{-2})	E (V)	If/Ib
POM-C_3N_4 NTs/GCE	8.11±0.08	0.87±0.01	5.39±0.02	0.68±0.03	1.50
C_3N_4 NTs/GCE	2.21±0.03	0.91±0.02	1.31±0.01	0.76±0.02	1.69

The measurements of constant-current discharge were performed at 75 mA m^{-2} by prepared electrodes in this work. Figure 3 indicates different profiles of discharge. The discharge potentials of POM-C_3N_4 NTs/GCE and C_3N_4 NTs/GCE are -0.47 and -0.35 V, respectively. Because the discharge potential of POM-C_3N_4 NTs/GCE is the more negative than that of POM-C_3N_4 NTs, its operational voltage can be higher. These results indicate that the nanocomposite performs a higher power density and faster reaction rate

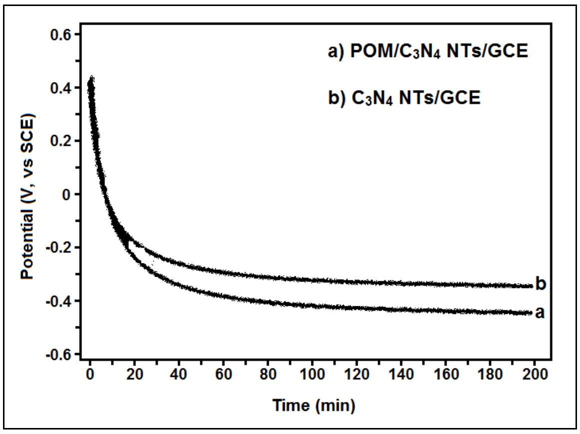

Figure 3: Potential-time curve of electrodes in 0.1 M phosphate buffer.

4 Conclusions

In present work, the novel nanocomposite including polyoxometalate and carbon nitride nanotubes was prepared for methanol oxidation. After various characterization studies, the electrochemical performances tests towards methanol were carried out. According to the test, the nanocomposite (POM-C_3N_4 NTs) performs a higher power density and faster reaction rate. Therefore, we can indicate that more clean energy and environments can be obtained by using the nanocomposite modified electrode. In addition, the electrochemical measurements show that the more effective catalyst is presented for fuel cell applications in the literature.

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