Conference materials
UDC 538.9
DOI: https://doi.org/10.18721/JPM.153.121

Facile fabrication of a TiO_2 NW-based glucose sensor by direct ink writing

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Abstract: This paper presents the results of facile fabrication of a non-enzymatic glucose sensor by forming a sensing element based on TiO_2 nanofilaments using direct ink writing (DIW). The glucose concentration in the solution was determined by changing the resistance of the TiO_2 layer. Nanowires (NW) were obtained by hydrothermal synthesis in 10 M sodium alkali solution followed by heat treatment. The surface morphology of obtained samples was studied using scanning electron microscopy. The formation of a sensitive layer was carried out on a 3D printer with a specially designed print head from a suspension based on an aqueous solution of polyvinyl alcohol (PVA) followed by heat treatment in air. The suspension was analyzed for viscosity and contact angle. The sensitive layers were formed on a silicon substrate with a SiO_2 surface oxide layer and gold contacts. Layers of TiO_2 NW were formed between the contacts. The sensitivity of the sensor to glucose solutions of various concentrations was studied. As a result of the studies, the studied structures showed sensitivity to a glucose solution in the range from 1 to 100 mmol.

Keywords: TiO_2, nanowires, hydrothermal synthesis, glucose sensor

Funding: This work was financially supported by the grant of President of the Russian Federation (project MK-2201.2021.4).

Citation: Tarasov A. M., Dubkov S. V., Gromov D. G., Ryazanov R. M., Volkova L. S., Facile fabrication of a TiO_2 NW-based glucose sensor by direct ink writing, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 15 (3.1) (2022) 125–130. DOI: https://doi.org/10.18721/JPM.153.121

Материалы конференции
УДК 538.9
DOI: https://doi.org/10.18721/JPM.153.121

Изготовление сенсора глюкозы на основе нанонитей TiO_2 методом робокастинга

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Аннотация. В данной работе приводятся результаты простого изготовления неферментативного сенсора глюкозы путём формирования чувствительного элемента сенсора на основе нанонитей TiO_2 методом робокастинга. Определение концентрации глюкозы в растворе происходило за счёт изменения сопротивления слоя TiO_2. Полученные структуры показали отклик на раствор глюкозы микромолярной концентрации.

Ключевые слова: TiO_2, нанонити, гидротермальный синтез, сенсор глюкозы

Финансирование: Исследование выполнено при финансовой поддержке гранта Президента Российской Федерации (проект МК-2201.2021.4).

Ссылка при цитировании: Тарасов А. М., Дубков С. В., Громов Д. Г., Рязанов Р. М., Волкова Л. С., Изготовление сенсора глюкозы на основе нанонитей TiO_2 методом робокастинга // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2022. Т. 15. № 3.1. С. 125–130. DOI: https://doi.org/10.18721/ JPM.153.121

Introduction

Today, biosensors are attractive objects for research due to their high sensitivity and high detection rate of substances with low concentrations, for example, the level of glucose in human blood. About 85 % of the market for modern glucose sensors is occupied by devices using electrochemical, chemiluminescent and phenylboronic acid-based glucose detection methods [1]. In recent years, FET-based sensors, which determine the concentration by changing the resistance when interacting with an analyte, are considered good candidates for creating glucose sensors. Most often, semiconductor materials (for example, ZnO [2], $BaTiO_3$ [3] or TiO_2 [4]) are used as a sensitive layer in such sensors. A particularly attractive option is using TiO_2 in the form of nanofilaments as a sensitive element of the sensor, due to its high stability and photocatalytic activity, which will allow to construct reusable sensors [5].

The creation of sensitive sensors is associated with difficulties in controlling their properties through using hybrid materials. Traditional methods of microelectronics are quite expensive and require highly qualified personnel. Additive technologies, in particular the method of direct printing from a solution (DIW), can provide an affordable alternative to traditional methods [6]. Additive technologies are introduced today in many areas, such as biomedicine, engineering and sensorics [7].

In this work, we demonstrate the formation of a sensitive layer of a glucose sensor by the DIW method based on TiO_2 NWs obtained by the hydrothermal method. A study of the surface morphology of the obtained TiO_2 nanowires was carried out, an approach to the formation of a sensitive layer was developed, and the sensitivity range of the sensor was identified. As a result, the developed sensor based on TiO_2 made it possible to detect glucose concentrations from 1 to 100 mmol.

Materials and Methods

Titanium dioxide NWs were obtained using the hydrothermal synthesis method. A stainless steel autoclave with a Teflon container was used to prepare 50 ml of 10 M NaOH solution (CAS number: 1310-73-2) and 0.6 mg of commercial TiO_2 powder (CAS number: 13463-67-7). The filling factor was 1/2. Then the autoclave was placed in a muffle furnace and heated to 250 °C. The synthesis time was about 12 hours. After synthesis was completed, the autoclave was cooled together with the oven to room temperature. The resulting nanowires were washed in a 0.1 M HCl solution (CAS number: 7647-01-0) with constant stirring to neutralize alkali residues and Na ions. To remove the acid, the NWs were washed in deionized water with heating to 60 °C and constant stirring. Washing was carried out to normal pH. Then the NWs were dried in air at 100 °C. At the final step, the obtained samples of NWs were heat treated at 700 °C for 4 hours in an air atmosphere. The structure morphology was studied using a Helios Nanolab 650 SEM microscope (20 kV, 10 pA). X-ray phase analysis of TiO_2 nanowires was carried out on a Malverin PanAnalytical Empirean diffractometer.

Ink was prepared for the formation of sensitive elements of the glucose sensor by the DIW method. The ink was based on an aqueous solution of polyvinyl alcohol (PVA). 20 g of PVA was added to 20 ml of deionized water and stirred until complete dissolution. Then, 20 mg of TiO_2 nanofilaments were added to the solution and sonicated for 1 minute using a Skymen JP-010T ultrasonic bath.

The viscosity of the suspension was measured with a VPZh-3 viscometer with a capillary diameter of 0.91 mm. Viscosity was measured at a constant temperature of 30 °C, which was provided by heating the viscometer case using a Lauda Alpha thermostat. The viscometer was filled with a PVA solution using a vacuum pump, then the solution was thermally stabilized for 10 minutes.

The contact angle was measured using an LK-1 goniometer. A drop of suspension with a volume of 0.5 μl was formed on the surface of a silicon wafer. After that, the goniometer focused on the drop and took a picture of the image. The resulting images were processed in the Drop Shape program.

A silicon wafer with SiO_2 on the surface about 300 nm thick was used as a substrate for the glucose sensor. Au-based contacts were formed by vacuum-thermal evaporation of a sample of the corresponding material (about 150 mg). The thickness of the obtained gold contacts was about 100 nm. The dimensions of the contacts were 1×1 mm^2, the step between the contacts was about 5 mm. The scheme for manufacturing contacts is shown in Figure 1, *a*.

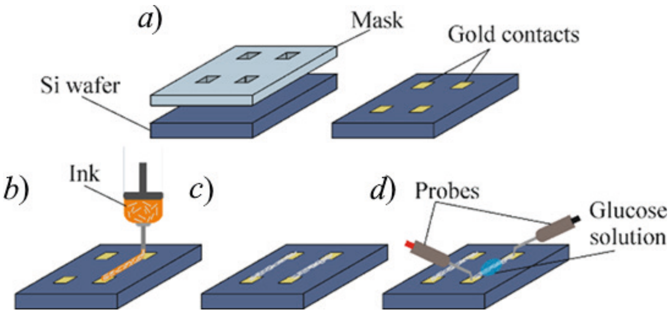

Fig 1. Scheme of sensor fabrication: deposition of gold contacts (*a*), formation of nanowire layer by the DIW method (*b*), polymer burning (*c*), measurement of the current-voltage characteristics of the sensitive layer with a glucose solution on the surface (*d*).

The formation of TiO_2 nanowires layers was carried out on a modified Anet A6 3d printer with a specially designed print head. A glass syringe with prepared ink was installed inside the print head (Fig. 1, *b*). A nozzle with a diameter of 0.4 mm was used for printing. Printing was carried out with a table temperature of 100 °C, and the water evaporated from the polymer in a few seconds. Next, the samples were annealed in air at a temperature of 600 °C for 10 minutes to remove the polymer (Fig. 1, *c*).

Study of the sensory properties of assets obtained by measuring the current-voltage characteristics. A drop of 10 μl of a transparent solution with a concentration of 5, 10, and 100 mM was applied with two gold contacts. Applying voltage to the Agilent e3647a power energy impact sensitive level. The current was measured with a Keithley 6485 picoammeter, and the voltage was measured with a Keithley 2700 multimeter. The measurement circuit is shown in Figure 1,*d*.

Results and Discussion

Figure 2, *a* shows the SEM image of TiO_2 NWs. The histogram of the length distribution of TiO_2 NWs is shown in Figure 2, *b*. Evidently, the length of the nanowires turned out to be fairly uniform. The predominant length of the nanowires was 8 μm.

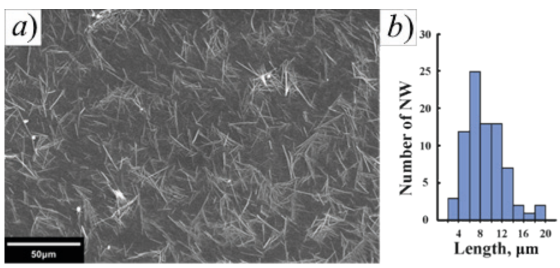

Fig. 2. SEM images of nanowires after 12 hours synthesis at 250 °C (*a*) and histograms of the size distribution of TiO_2 NWs (*b*)

Figure 3 shows X-ray diffraction (XRD) of the synthesized nanowires before and after annealing. The unannealed nanowires do not exhibit the peaks characteristic of anatase and rutile. After synthesis, $Na_2Ti_3O_7$ is formed, which, when washed with hydrochloric acid, passes into $H_2Ti_3O_7$, whose peaks are observed at 24.8° and 48.5° [8]. Annealed nanowires exhibit peaks characteristic of ananthase and rutile.

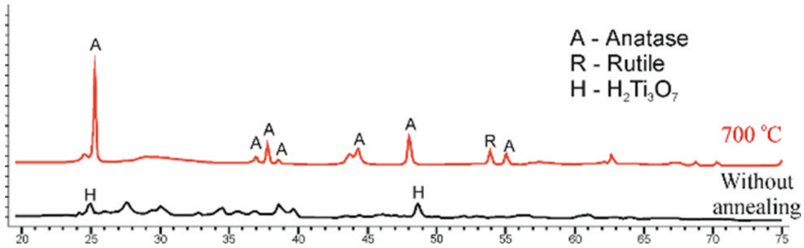

Fig. 3. X-ray diffraction (XRD) of TiO_2 NWs before and after annealing

The measured viscosity of the PVA solution showed a value of 19.44 mm^2/s. The viscosity of water at 30 °C is 0.8 mm^2/s. The addition of PVA to the ink allows the use of aqueous solutions for DIW printing. The edge wetting angle of the PVA solution was 46 °, which is less than that of water. However, the evaporation of water from the solution is faster, so there is no strong spreading of the ink.

Figure 4, *a* shows the SEM image of the formed layers of TiO_2 nanowires. With a nozzle diameter of 0.4 mm, the resulting line thickness is approximately 0.7 mm. This can be attributed to the spreading of ink over the surface of the silicon substrate before the water evaporates. After annealing in air (Fig. 4, *b*), cracking of the layer is observed as a result of polymer boiling.

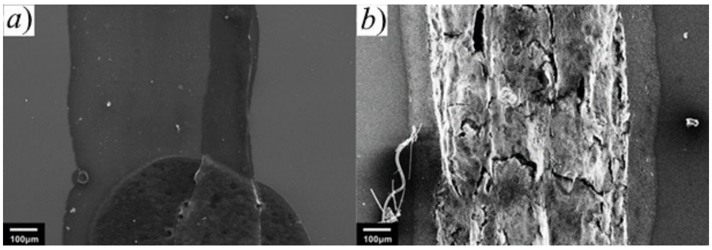

Fig. 4. SEM images of TiO_2 NW layer formed by DIW method before annealing (*a*) and after annealing (*b*)

At a higher magnification (Fig. 5), we can see that the NWs have a predominant direction, which coincides with the direction of movement of the print head. This effect occurs due to the friction that occurs in the nozzle in a viscous medium. For sensing applications, this can be beneficial as it increases the chance of making a contact with nearby nanowires [9].

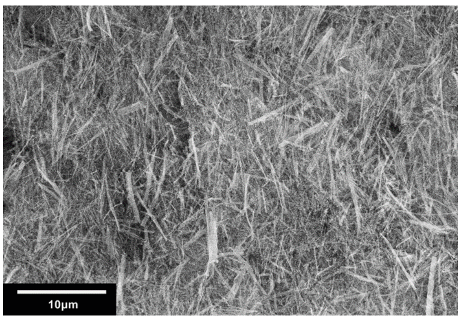

Fig. 5. SEM image of TiO_2 nanowire layer formed by DIW method after annealing

The study of the current-voltage characteristics of sensitive layers at different concentrations of glucose solution showed the results presented in Figure 6. With an increase in the concentration of glucose solution, the conductivity of the structure increases. This effect can be explained by the doping of the TiO_2 surface with glucose, which plays the role of an electron donor. This increases the conductivity of the sensitive layer [10].

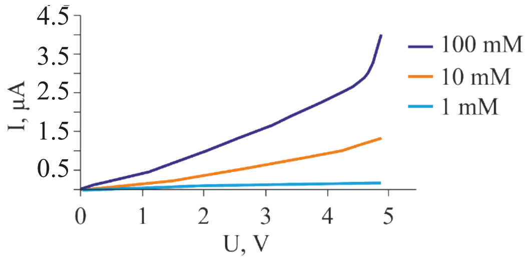

Fig. 6. Volt-ampere characteristic as a function of glucose concentration

Conclusion

In the course of this work, we synthesized TiO_2 nanowires with a length of about 8 μm and a diameter of about 200 nm. An approach using an Anet A6 3D printer was developed to form sensitive sensor layers using the direct ink writing method based on a TiO_2-PVA suspension. The developed suspension based on the TiO_2-polymer has a contact angle of 46° and a viscosity of about 19.44 mm^2/s. A glucose sensor based on TiO_2 nanowires formed by the DIW method made it possible to detect the concentration of a glucose solution from 1 to 100 mM. Additive technology methods make it easy to form functional layers for sensors of arbitrary shape without involving expensive equipment. Using TiO_2 as a sensitive element of the sensor in the future will allow us to study the effect of self-cleaning of the surface of the glucose sensor and create a structure with the option for reuse.

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Received 22.05.2022. Approved after reviewing 07.07.2022. Accepted 07.07.2022.