METHOD FOR MANUFACTURING THIN FILMS OF CUBI$_2$O$_4$
FOR PHOTOELECTROCHEMICAL APPLICATIONS

Abstract. A method has been developed for producing thin semiconductor films of a complex copper-bismuth system (CuBi$_2$O$_4$) with reduced roughness and increased photoactivity.

The application process is carried out under standard laboratory conditions from aqueous solutions of salts, takes advantage of centrifugation to evenly distribute the coating over the surface, is characterized by low material consumption, and allows the thin nanocrystalline layers formation with a given thickness. Polyethylene glycol (PEG) is used to improve the spraying of solution droplets over the entire surface of the CuBi$_2$O$_4$ film, which allows the dense uniform films deposition.

Scanning electron and atomic force microscopy data demonstrate the ordering of the growth of CuBi$_2$O$_4$ particles (size ~200 nm) and a 1.5-fold decrease in the roughness of the relief when polyethylene glycol is added to the solution. Micrographs show the growth of uniformly sized rounded crystallites.

In a comparative analysis of the XRD diagram of the samples, an increase in the number and intensity of peaks corresponding to the crystalline phase of Kusachie (CuBi$_2$O$_4$) with the introduction of PEG into the initial solution is observed.

Based on the photoelectrochemical measurements results, it was found that the addition of polyethylene glycol to the electrolyte helps to increase the photoactivity of the samples by 2 times.

The obtained thin polycrystalline CuBi$_2$O$_4$ films are promising for use in photoelectrochemical converters.

Keywords: Solar energy material, spin coating, CuBi$_2$O$_4$, polyethylene glycol.

Introduction. A fundamental condition for a hydrogen economy is the ability to renew, purify, and efficiently produce hydrogen.

Currently, non-renewable methods for producing hydrogen, such as steam methane conversion, are cheaper than photoelectrolysis. However, the methane process leads to CO$_2$ emissions and is ultimately limited to natural gas reserves. On the contrary, photoelectrolysis of water does not lead to environmental pollution, sunlight and water can be considered inexhaustible resources, and with an increase in the efficiency of use of solar energy, it can be expected that internal costs will continue to decrease [1].

A significant advantage of the hydrogen obtained by photoelectrolysis is the relative ease of storage. If necessary, hydrogen can be stored and then converted into electricity in a fuel cell, which makes it particularly advantageous as a fuel for transport or in remote locations without electricity. In addition, it can simply be burned as fuel for heating or cooking, making it a promising alternative to natural gas.

However, despite significant research efforts over the past decades, fundamental problems still impede the commercial use of photovoltaics. Such problems include the low efficiency of sunlight, the corrosive instability of most semiconductors in aqueous solutions, the complex and expensive designs of PEC elements, etc. Obviously, to achieve progress, innovation is needed in both device design and material development.

One of the materials that can provide a high photocurrent density and a large overvoltage of the process of water photolysis is CuBi$_2$O$_4$, which was first proposed as a possible photocathode material in
CuBi$_2$O$_4$ is a p-semiconductor and has many promising physico-chemical properties including magnetic susceptibility, dielectric constant, high-temperature heat capacity, electrochemical capacitance, photoelectrochemical ability and catalytic properties [5-7]. CuBi$_2$O$_4$ has a small energy of the band gap of 1.5-1.9 eV, and, therefore, can largely absorb the visible parts of the solar spectrum [8-11]. The potential of the conduction band of CuBi$_2$O$_4$ is more negative than the redox potential of H$^+/H_2$. Due to this, CuBi$_2$O$_4$ is widely studied for use as a photocathode for solar energy and decomposition of water with evolution of hydrogen [12-17]. CuBi$_2$O$_4$ can be used as a promising photocatalyst for the decomposition of organic pollutants and dyes [17].

In recent years, many methods of obtaining CuBi$_2$O$_4$ have been used. Crystalline CuBi$_2$O$_4$ nanoparticles were synthesized using various methods, including solid-phase reactions [8,9,18], mechanochemical treatment [19-20], hydrothermal crystallization [21-23], thermal decomposition and complexation [24,25], microwave synthesis [6], ultrasonic method [16], electrochemical synthesis [13,26], magnetron sputtering [28], floating zone method [29], and sol-gel method [30]. Most of these methods are not widely used due to complexity, the use of high temperatures and low reproducibility.

In this work the spin coating method was used, which is carried out under standard laboratory conditions from aqueous salt solutions, uses the advantages of centrifugation to uniformly distribute the coating on the surface, is characterized by low material consumption, allows the formation of thin nanocrystalline layers with a given thickness. It is known that the addition of polymers is often used to the uniform distribution of solution droplets over the entire surface of the deposited films when using the spin-coating method. In this work polyethylene glycol (PEG) is used for this purpose. The investigations of photoelectrochemical properties of CuBi$_2$O$_4$ thin films are important for the creation of effective photocathodes.

**Experimental procedure.** A solution for depositing CuBi$_2$O$_4$ films was prepared by mixing copper nitrate trihydrate and bismuth nitrate pentahydrate (at 0.05M and 0.1M, respectively) with acidification with concentrated (65%) nitric acid. Subsequently, the resulting mixture was evaporated without boiling to an amount of 1/5 of the original volume and cooled to room temperature. The preparation of solutions containing polyethylene glycol - 2000 (PEG) additives was performed after cooling the initial solution, adding PEG in the amount of 0.25 grams to each 5 ml of the solution. After that, the solution was subjected to treatment in an ultrasonic bath. The resulting mixture was used for at least an hour, but not later than a day after preparation.

Films of the complex system copper-bismuth were obtained by the spin coating method. The films were applied to pre-cleaned optically transparent electrodes, which are a fluorinated tin oxide glass (FTO), measuring 10*25 mm. During rotation of the FTO, the electrodes were fixed in the horizontal plane by a special holder, which avoided the displacement of the substrate and eliminated the influence of the position on the uniformity of film deposition. Rotation lasted 90 seconds at a frequency of 500 rpm.

After application, the films were annealed in a muffle furnace for 2 hours at a temperature of 600°C.

In the future, physico-chemical characterization of all samples was carried out.

With the help of an electronic scanning microscope from JEOL (Japan) with the capabilities of the micro analysis "JSM 6610LV", surface micrographs were obtained. Analysis of the elemental composition excluded the presence of impurities.

The structure and morphology of the surface were studied by atomic force microscopy (JSPM-5200 (JEOL)). During the measurements, images of topography and contrast images for the phase regions were recorded. During scanning, a region measuring 500x500 nm was examined.

The crystal structure was confirmed by X-ray diffraction on the X-ray diffractometer DRON-4-07.

Photoelectrochemical studies were performed in real time in a solution of 0.2 M Na$_2$SO$_4$ + 0.1 M phosphate buffer + 10 mM H$_2$O$_2$ under modulated illumination with a wavelength of 465 nm in a GillAC (ACM Instruments) apparatus using a quartz cuvette and a silver chloride reference electrode.

**Results and Discussion.** Figure 1 compares the results of electron microscopy for CuBi$_2$O$_4$ films deposited on FTO/glass from solutions without organic constituents (Fig. 1a, c) and from solutions containing PEG (Fig. 1b, d). Microphotographs of the samples surface show that the addition of polyethylene glycol to the solution contributes to the ordered growth of identical in size and shape grains...
(190-210 nm), while precipitation from the primary solution observed the development of chaotic formations ranging in size from 85 nm to 820 nm and the presence of significant relief changes.

Figure 1 - SEM micrographs of the surface of deposited CuBi$_2$O$_4$ films a, c) without using PEG; b, d) in the presence of PEG

The results of elemental analysis show that the elemental composition of the films corresponds to the composition of the CuBi$_2$O$_4$ precipitate with an accuracy of ± 2 at %. The introduction of polyethylene glycol into the solution does not affect the composition change and does not contribute to the appearance of impurities in the composition of the precipitate.

Figure 2 shows the results of films investigation on an atomic force microscope. On scans in 3D format, growth figures up to 146 nm (figure 2a) are formed from the initial solution, whereas for films deposited from solutions with polyethylene glycol content only growth up to 94 nm is observed (figure 2b). Experiments showed that when using a solution with PEG, the roughness of the surface decreases by a factor of 1.5, and the crystallites have a rounded shape characteristic of the CuBi$_2$O$_4$ compound.

Figure 2 - Micrograph of surface obtained on AFM for deposited CuBi$_2$O$_4$ films a) without using PEG; b) in the presence of PEG
Figure 3 shows the X-ray diffraction patterns of CuBi$_2$O$_4$ films deposited on glass/FTO from the initial solution (figure 3a) and solutions containing PEG (figure 3b). Crystallographic analysis of X-ray data and EDAX measurements confirm the presence of the Kusachiite phase (CuBi$_2$O$_4$). The peaks of SnO$_2$ from the substrate on the diffraction diagrams are due to the small thickness of deposited CuBi$_2$O$_4$ films (less than 500 nm).

From the results of XRD it is obvious that the introduction of polyethylene glycol into the solution positively affects the film structure. There is an increase in the diffraction peaks and their intensities.

The photosensitivity of the deposited CuBi$_2$O$_4$ films was studied by photoelectrochemistry with modulated illumination with a wavelength of 465 nm (a solution of 0.2 M Na$_2$SO$_4$ + 0.1 M phosphate buffer + 10 mM H$_2$O$_2$). Figure 4 shows the photocurrent curves for samples of CuBi$_2$O$_4$ thin films.
Photoelectrochemical study of deposited films showed that the photocurrents are negative, and the resulting semiconductor is characterized by a p-type conductivity. A comparison of the photocurrent values indicates that the photoelectrochemical activity of films deposited from solutions containing polyethylene glycol was found to be 2 times higher when switching from the light off mode to the light on mode (figure 4b) than the precipitated ones without the addition of PEG (figure 4a).

The developed method of deposition of a complex copper-bismuth CuBi$_2$O$_4$ system allows obtaining photocathodes with high photosensitivity.

**Conclusion.** A new composition of a solution for the thin films deposition of the copper-bismuth (CuBi$_2$O$_4$) complex system on FTO/glass by the spin coating method has been developed.

The physicochemical characterization of samples precipitated from solutions containing and without polyethylene glycol was carried out. The positive effect of the use of PEG is shown.

Surface micrographs showing the ordering of the growth of CuBi$_2$O$_4$ particles (size ≈200 nm) with the addition of polyethylene glycol to the solution were obtained by SEM.

The results of AFM indicate a 1.5 times decrease in the roughness of the relief and the formation of equidimensional rounded crystallites.

For all films, the XRD method confirmed the presence of the crystalline Kusachiite phase corresponding to the CuBi$_2$O$_4$ compound. Comparative analysis of the XRD diagram of samples obtained from solutions containing PEG and "pure" (without PEG) shows an increase in the number of peaks and their intensity in the first case.

Based on photoelectric measurements, it is established that CuBi$_2$O$_4$ films precipitated from solutions containing polyethylene glycol show a photoactivity of 2 times higher.

Thus, the developed method of deposition of a complex copper-bismuth CuBi$_2$O$_4$ system makes it possible to obtain polycrystalline films with high photosensitivity, p-type conductivity, which are promising for use in photoelectrochemical converters as photocathodes.
(ПЭГ) бар еритінділерден кабыкшаларының тұндыру және тәріздесті эксперименттер ушін еритіндіге әрбір 5 мл еритіндіге 0,25гр ПЭГ-2000 қосылы. Тіімді арақастьру ушін ултұралдықтың ванна қолданылыды. Эксперимент нәтижелері дайындалған ерітіндінің тіімді пайдалану мерзімі дайындағаннан кейін бір тәуелді артық болмаса керсеті.

Соғыс кезекте муфельді пеште кабыкшаларды 2 сағат бойы 600°C температурала қуйдіру және таңаға асырылды.

Физикалық-химиялық зерттеулердің нәтижелері электролиттерден жасалған үлгілердің қосындысынан мүмкін болатындығы айырмашылықтарды анықтады.

Сканерлі электрондық және атомдық-куш микроскопияның дәлілдері CuBi2O4 белшектердін ретке тәріздігін (келем -200 нм) және еркінде полиэтиленгликоль қосылған кезде рельефінің 1,5 есе темендеуін керсетеді. Микрофотографияда біркелкі елшемді денгелек кристалдардың есі байқалады.

Бастақты ерітіндіге ПЭГ енгізгенде үлгілердің XRD диаграм салыстырмалы талдауында kusachiite (CuBi2O4) кристалдық фазасына сәйкес байқалады.

Фотоэлектрохимиялық елшеулердің нәтижелерінде электролитке полиэтиленгликольді қосу үлгілердің фотоактивтілігін 2 есе арттыруға ықпал етеді.

Осындай, фотоэлектрохимиялық түрлендірілік теріс Si негізінде электролитке полиэтиленгликольді қосу үлгілердің фотоактивтілігін 2 есе арттырудың мүмкін болуы мүмкіндік береді.

Тірек сөздер: күн энергиясы матеріалдары, spin coating, CuBi2O4, полиэтиленгликоль.
Результаты физико-химических исследований выявили значительные отличия в образцах, изготовленных из электролитов с различным содержанием ПЭГ.

Данные сканирующей электронной и атомно-силовой микроскопии демонстрируют упорядочивание роста частиц CuBi2O4 (размер ≈200 нм) и снижение в 1,5 раза шероховатостей рельефа при добавлении в раствор полиэтиленгликоля. На микрофотографиях виден рост равноразмерных округлых кристаллитов.

При сравнительном анализе XRD diagram образцов, наблюдается увеличение количества и интенсивности пиков, соответствующих кристаллической фазе Kusachite (CuBi2O4) при введении ПЭГ в исходный раствор.

На основании результатов фотоэлектрохимических измерений установлено, что добавление в электролит полиэтиленгликоля способствует увеличению фотоактивности образцов в 2 раза.

Таким образом, разработанная методика осаждения сложнооксидной системы медь-висмут CuBi2O4 позволяет получать поликристаллические слои p-типа проводимости с высокой фоточувствительностью, перспективные для использования в фотоэлектрохимических преобразователях.

**Ключевые слова:** материалы для солнечной энергии, spin coating, CuBi2O4, полиэтиленгликоль.

**Information about authors:**
Puzikova Darya Sergeevna - PhD student, master’s degree, researcher in electrochemical laboratory of JSC “D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry, d.puzikova@ifce.kz, https://orcid.org/0000-0001-5275-4769
Dergacheva Margarita Borisovna - doctor of chemical science, professor, chief researcher in electrochemical technology laboratory of JSC “D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry”, m_dergacheva@mail.ru, http://orcid.org/0000-0002-8490-1601
Khussurova Gulinur Marsovna - master’s degree, Junior Researcher in electrochemical technology laboratory of JSC “D.V. Sokolskiy Institute of Fuel, Catalysis and Electrochemistry, gulinur_k@bk.ru, https://orcid.org/0000-0001-8700-7472

**REFERENCES**


