# RESEARCH OF PHOTOELECTROCHEMICAL PROPERTIES OF $CuBi_2O_4$ BASED PHOTOCATHODES AND THEIR MODIFICATION BY SILVER IONS ON CONDUCTIVE GLASSES

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***ABSTRACT***

The article presents the results of the study of photo electrochemical properties of copper-containing photocathodes on conductive glasses by aqueous solutions pyrolysis and electrochemical method. All electrodes showed absorption in the entire range of the visible spectrum, starting from 330 nm and above, at that silver alloying of copper bismuthate results in decrease in optical density of the electrodes, which is accompanied by a large value of current indicators. It is shown that cathodes based on copper oxide have minimal photocurrents, whereas triple copper oxide based on copper bismuthate shows much better indicators at aqueous solutions electrolysis. This may be due to intensification of main carriers tunneling process at concentration points of silver ion centers in an array of copper bismuthate film. This is due to additional current component in general voltage–ampere characteristic of the electrode, i.e. the current is ultimately higher for the sample with silver ions than without it. Almost fivefold increase in photocurrents on the electrodes of copper bismuthate doped with silver ions in the sacrificial electrolyte has been achieved.

**Keywords:** photocurrent, photocathode, band gap, copper bismuthate, absorption spectrum, aerosol method.

## *INTRODUCTION*

Photo electrolysis of water on semiconductor substrates with hole conductivity, so-called photocathodes, is one of the ways to produce hydrogen. Copper oxides are ones of the most studied, widespread and at the same time cheap materials of photocathodes. CuO and $Cu_2O$ are p-type metal oxide semiconductors due to their remarkable optical, electrical, thermal and magnetic properties [1-2]. A number of methods for synthesis of materials for development of gas sensors with the use of semiconductors and nanostructures of p-CuO have been reported in the literature. They are methods of solvathermal and thermal evaporation, hydrothermal and microwave hydrothermal, ultrasonic spray pyrolysis and electrodeposition. The sensors were also made as nanowires, nanorods, mesoporous films, nanocubes, nanosolders, nanotubes and nanoribbons, hollow spheres, etc. [3-5].

On the other hand, it is more interesting to study complex (more than three elements) copper-containing photocathodes, such as $CuBi_2O_4$ (copper bismuthate). p-type metal oxides are attractive because they can easily exchange their lattice oxygen with air to maintain their stoichiometry due to formation of phase-segregated domains in films with stoichiometric non-perfection. This is very useful property for maintaining long-term stability of photoelectrodes in the oxidizer aqueous environment. In addition, $CuBi_2O_4$ nanostructuring can additionally improve characteristics of this important functional material and give it unique properties that are not present in its bulk form. In particular, triple oxides should have more diverse

properties, for example, in other devices (sensors and devices), which may differ significantly depending on components ratio in CuO/Me/O system [6-9]. $CuBi_2O_4$ (CBO) is one such example, whose band gap is suitable for sunlight (1.5–1.8 eV) with relatively positive value of the valence band in the electrode potential scale, which makes it an attractive candidate for $CO_2$ reduction [10-19].

## *MATERIALS AND METHODS*

The following reagents were used for research: copper acetate $Cu(CH_3COO)_2 \cdot H_2O$, bismuth nitrate $Bi(NO_3)_3 \cdot 5H_2O$ according to GOST 4110-75, concentrated nitric acid, acetone and alcohol. To prepare copper acetate solution A, 1 g of salt was dissolved in 50 ml of water, which corresponds to 2% solution. Solution A was sprayed onto conductive glass. Coating of conductive glasses was carried out as follows: a layer of solution A was applied to the heated substrate, after which the substrate was dried, heated again to a temperature of 100-120$^0$C, and the cycle was repeated. Such layers were applied 10, 20 and 30 times, after which the substrate was finally annealed for 1 hour at a temperature of 500$^0$C. 0.01% bismuth nitrate solution B acidified with nitric acid was used to apply bismuth coatings. Acetone was used for degreasing conductive glasses. The copper acetate coating procedure was similar to the above scheme.

Samples of the following composition were prepared this way:

1. Obtaining CuO sample by spraying copper acetate solution on conductive glass in 10, 20 and 30 spray application cycles followed by annealing at 500$^0$C.

2. 2 ml of solution A and 3 ml of solution B were mixed and then applied to the glass according to the above procedure.

3. 0.5 ml of $CuCl_2 \cdot 2H_2O$ solution was mixed with 5 ml of solution B with a complexion; this mixture was applied electrochemically to a conductive glass for 60 seconds [20], i.e. a layer of copper bismuthate was formed.

4. 2 ml of solution A and 3 ml of solution B were mixed, 0.01 ml of 0.025 M $AgNO_3$ solution was added to the mixture; the formed solution was applied to the glass according to the procedure described in paragraph 1.

To obtain coatings on the conductive glass, FTO glasses (conductivity less than 15 ohm /cm$^2$) of the Singapore company LATECH were used with a size of 1x2.5 cm$^2$, which were degreased in soda ash solution and by ultrasound, washed sequentially in isopropanol, acetone and dried. Two types of electrolytes were used for photoelectrochemical studies: neutral in the form of 0.1M solution of $KH_2PO_4$, as well as complex electrolyte in the form of 0.1 M $KH_2PO_4$ solution with addition of 0.1 M $H_2O_2$ solution in the form of a so-called "sacrificial" solution. The scheme for measuring photoelectrochemical characteristics of films is shown in Fig. 1.

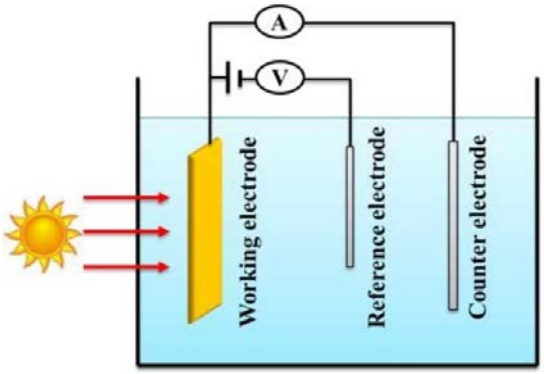


Fig. 1. Three-electrode scheme for measurement of photoelectrochemical characteristics

Microphotographs of films were taken with the use of JSM-6490LV scanning electron microscope (JEOL, Japan). Absorption spectra of copper bismuthate on the conductive glass were obtained using Cary-50 UV-visible area Spectrophotometer.

***RESULTS AND DISCUSSION***

Fig. 2 shows optical characteristics of copper bismuthate electrodes at 10 cycles of application to the substrate with a spray gun.

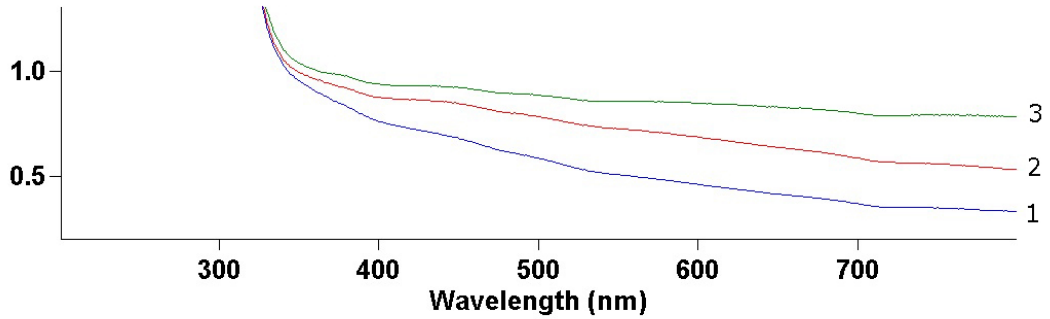


Fig. 2. Absorption spectra of copper bismuthate at application by: aerosol method (1), electrochemical method (2), aerosol method in the presence of silver ions (3)

It can be seen in Fig. 2 that all samples show the main absorption band, starting from the absorption edge in the size of 330 nm, which expands and amplifies into the long-wavelength part. Spectra of copper bismuthate obtained by pyrolysis of aqueous solutions of corresponding salts 20 mM $Cu(NO_3)_2 \cdot 3H_2O$ and 40 mM $Bi(NO_3)_3 \cdot 5H_2O$ with subsequent annealing at $450^0$C are presented in [19]. The authors show that the sample begins to absorb already at an initial absorption of ~ 1.51 eV. Consequently, the width of $CuBi_2O_4$ band gap at spray pyrolysis is defined as being in the range of 1.41-1.50 eV, which is at the lower limit of the previously reported values (1.5-1.8 eV). In our case, the sample absorbs in the entire region of the spectrum, starting from 330 nm, which corresponds to the absorption boundary

from 3.7 eV and so on. Further, the difference between aerosol and electrochemical deposition methods increases as one moves to the region of higher wavelengths, i.e. there is a splitting between lines 1, 2, and 3. The absorption of an "electrochemical" sample is generally lower than that of an "aerosol" sample at large numbers of wavelengths.

Surprisingly, a decrease in absorption of the sample with silver addition is detected (although the opposite effect was expected), which can be explained by an increase in main carriers tunneling process at concentration points of silver ion centers in an array of copper bismuth film. This apparently leads to additional current component in general voltage–ampere characteristic of the electrode, i.e. the current is ultimately higher for the sample with silver ions. As a result, we see that the final current characteristic of the electrode is higher than that for the electrode without silver ions. We called this the additional generation of electron-hole pairs in centers of silver ions as part of copper bismuthate, which ultimately leads to increasing current characteristics of the electrodes.

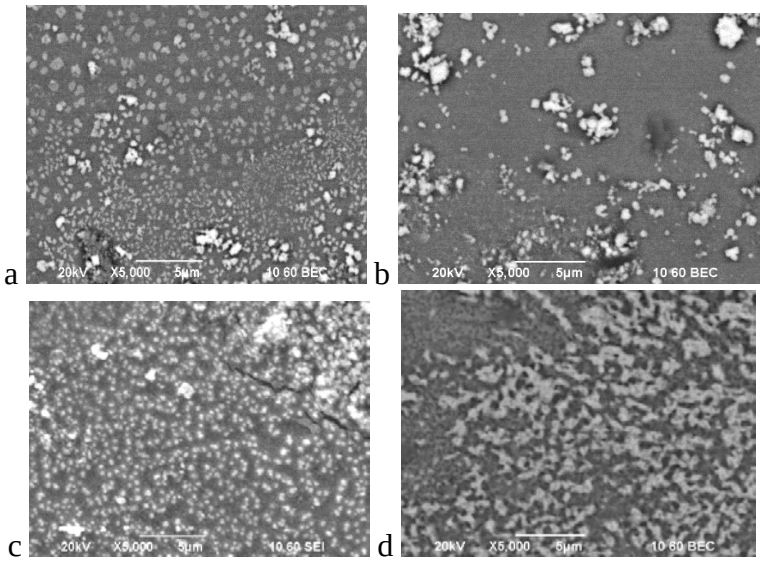


Fig. 3. Micrographs of copper bismuthate at various application cycles: “electrochemical” copper bismuthate with 10 application cycles (a), “aerosol” copper bismuthate with 10 application cycles (b), “electrochemical” copper bismuthate with 30 application cycles (c), “aerosol” copper bismuthate with 30 application cycles (d)

Microphotographs show that the more layers of the coating applied, the stronger the continuity of the samples is. On the other hand, the morphology of copper bismuthate layer differs for the samples: it can be seen that the “aerosol” sample with copper bismuthate is looser in structure than the “electrochemical” one. There is also such a feature that, despite the lack of continuity, all samples give tangible current characteristics (see below).

Fig. 4 shows the current characteristics of various electrodes in a neutral phosphate electrolyte. It can be seen that minimum photoelectrochemical characteristics are inherent for copper oxide layer, and quantitatively these are currents of no more than 12 mkA. But for the electrodes of “aerosol” copper bismuthate, the current doubles by more than 2-2.5 times. Moreover, for convenience, the current for cathode potential region is shown, which indicates that all electrodes have p-type of conductivity. The current increases significantly for “electrochemical” electrodes (curve 3) and especially for a sample with silver addition (curve 4). The currents at that reach values of 50-60 mkA.

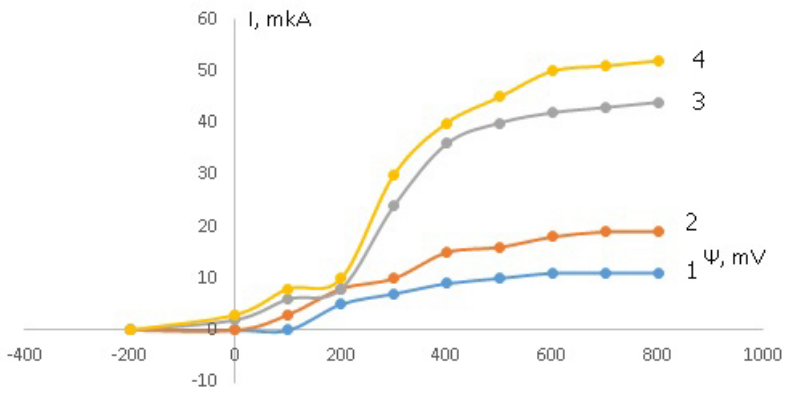


Fig. 4 - Current characteristics of photoelectrodes in phosphate electrolyte: CuO (1), $CuBi_2O_4$ "aerosol" (2), $CuBi_2O_4$ "electrochemical" (3), $CuBi_2O_4$+Ag "electrochemical" (4)

The dependence of photocurrents for a sacrificial electrolyte is more indicative (numbering of samples is unchanged), but the currents are much bigger, more than 4-5 times (Fig. 5). In this case, the beginning of cathode photocurrents is shifted for all electrodes by 200 mV to the negative region.

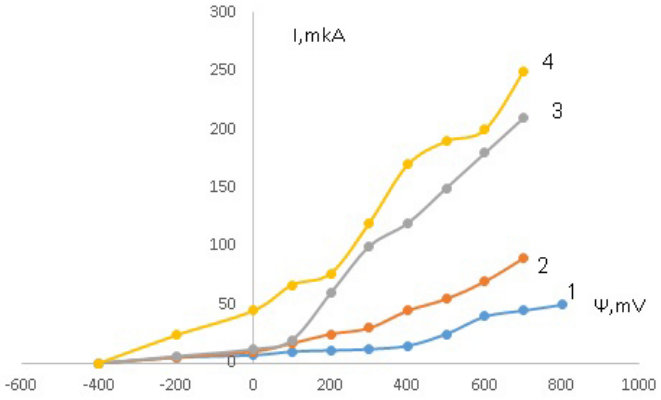


Fig. 5. Current characteristics of photoelectrodes in sacrificial electrolyte: CuO (1), $CuBi_2O_4$ "aerosol" (2), $CuBi_2O_4$ "electrochemical" (3), $CuBi_2O_4$+Ag "electrochemical" (4)

It is obvious that the electrode morphology also affects the efficiency of photoelectrolysis, which ultimately explains recombination processes. Fig. 3 clearly shows that the samples differ both in morphology and porosity. It is obvious that porous morphology can give a larger area for photoelectrochemical reaction than dense morphology by reducing recombination of charges on the surface of photoelectrodes. In contrast, porous morphology can also narrow the electron transfer passages at the boundaries between photocatalyst particles to increase recombination charge inside the electrodes. In future, it is necessary to research the relationship between electrodes morphology and activity for photoelectrochemical increase of hydrogen. In our case, it is necessary to compare layers of

$CuBi_2O_4$ electrodes by morphology and density in a larger range of parameter variation when using electrodes and prepare samples for better identification of the compared parameters, for example, as done by authors [21]. It is also indicative the comparison of e main photoelectrochemical (PEC) functions, as well as the ability to systematically analyze on a number of copper vanadate photoanodes with different ratio of Cu:V elements [22]. One thing is certain – this topic of "porosity and morphology" should be studied more scrupulously and with the use of additional analysis methods.

## *CONCLUSION*

Photoelectrochemical properties of copper-containing photocathodes on conductive glasses have been studied by pyrolysis of aqueous solutions and by electrochemical method, wherein silver alloying of copper bismuthate results in a decrease in the optical density of the electrodes. It is however accompanied by a large value of current indicators. It is shown that in comparison with initial copper oxide, modification of solutions with bismuth is accompanied by the formation of complex Cu-V-O oxides, and the best current characteristics are obtained for Cu-V-O system when coating in the current coating mode, i.e. in the “electrochemical” mode. An almost fivefold increase in photocurrents on copper bismuthate electrodes doped with silver ions was obtained, which is associated with additional generation of electron-hole pairs in the centers of silver ions in the composition of copper bismuthate.

## *REFERENCES*

1 Smirnov A.V., Vasiliev A.I., Platonov P.S., Stolbov D.O., Tsareva E.R., Sorokin G.M., Tunterov E.S., Petrov D.V. Sintez I issedovanie gazochuvstvitelnyh svoistv tonkih plenok oksida medi [Synthesis and study of gas sensitive properties of copper oxide thin films]. *Prikladnaya fizika – Applied Physics*, 2020, no. 1, pp. 53- 57.

2 Sun C., Su X., Xiao F., Niu C. Synthesis of Nearly Monodisperse $Co_3O_4$ Nanocubes via a Microwave-assisted Solvothermal Process and Their Gas Sensing Properties. *Sensors Actuators B: Chem*, 2011, vol. 157, no. 2, pp. 681-685.

3 Yang C., Su X., Xiao F., Jian J., Wang J. Gas Sensing Properties of CuO Nanorods synthesized by a Microwave-Assisted Hydrothermal Method. *Sensors Actuators B: Chem*, 2011, vol. 158, no. 1, pp. 299-303. DOI: 10.1016/j.snb.2011.06.024

4 Singh I., Bedi R. K. Effect of the annealing temperature on crystalline phase of copper oxide nanoparticle by copper acetate precursor and sol–gel method. *Journal of Thermal Analysis and Calorimetry*, 2014, vol. 115, pp. 419–423.

5 Kincal D., Kumar A., Child A.D., John R., Reynolds J.R. Conductivity switching in polypyrrole-coated textile fabrics as gas sensors. *Synthetic Metals*, 1998, vol.92, no. 1, pp. 53-56. doi.org/10.1016/S0379-6779(98)80022-2

6 Seitmagzimov A.A., Seitmagzimova G.M., Seitmagzimova L.A. Aerosol method for obtaining thin films of doped bismuth vanadate for water photolysis. *Industrial Technology and Engineering*, 2021, no. 3 (40), pp. 44-52.

7 Sahoo P.P., Zoellner B., Maggard P.A. Optical, electronic, and photoelectrochemical properties of the p-type $Cu_3{-}xVO_4$ semiconductor. *J. Mater. Chem.* A, 2015, no. 8, pp. 4501−4509.

8 Lalanne M, Barnabe A., Mathieu F., Tailhades Ph. Synthesis and thermostructural studies of a CuFe(1-x)Cr(x)O(2) delafossite solid solution with 0. *Inorg. Chem*, 2009, vol. 48, no. 13, pp. 6065−6071. doi: 10.1021/ic900437x

9 Sullivan I., Sahoo P.P., Fuoco L., Hewitt A.S., Stuart S., Dougherty D., Maggard P.A. Cu-Deficiency in the p-Type Semiconductor $Cu_5{-}xTa_{11}O_{30}$: Impact on Its Crystalline Structure, Surfaces, and Photoelectrochemical Properties. *Chem. Mater*, 2014, vol. 26, 23, pp. 6711−6721. doi: 10.1021/cm502891t

10 Cao D., Nasori N., Wang Z., Mi Y., Wen L., Yang Y., Qu. S., Lei Y. p-Type $CuBi_2O_4$: an easily accessible photocathodic material for high-efficiency water splitting. *J. Mater. Chem. A*, 2016, 23, 4, 8995-9001.

11 Yang J., Du C., Wen Y., Zhang Z., Cho K., Chen R., Shan B. Enhanced photoelectrochemical hydrogen evolution at p-type $CuBi_2O_4$ photocathode through hypoxic calcination. *Int. J. Hydrogen Energy*, 2018, vol. 43, pp. 9549-9557. doi: 10.1016/j.ijhydene.2018.04.066.

12 Li J., Griep M., Choi Y.S., Chu D. Photoelectrochemical overall water splitting with textured $CuBi_2O_4$ as a photocathode. *Chem. Commun*, 2018, 54: 3331–3334. doi: 10.1039/C7CC09041B.

13 Berglund S.P.; Lee H.C., Nunez P.D., Bard A.J., Mullins C.B. Screening of transition and post-transition metals to incorporate into copper oxide and copper bismuth oxide for photoelectrochemical hydrogen evolution. *Phys. Chem. Chem. Phys*, 2013, vol.13, pp. 4554-4565.

14 Lahmar H., Benamira M., Akika F.Z., Trari M. Reduction of chromium (VI) on the hetero-system $CuBi_2O_4/TiO_2$ under solar light. *J. Phys. Chem. Solids*, 2017, vol. 110, pp. 254-259. doi: 10.1016/j.jpcs.2017.06.021

15 Guo F., Shi W., Wang H., Huang H., Liu, Y., Kang, Z. Fabrication of a $CuBi_2O_4/g\text{-}C_3N_4$ p-n heterojunction with enhanced visible light photocatalytic efficiency toward tetracycline degradation. *Inorg. Chem. Front.*, 2017, vol. 10, pp. 1714-1720.

16 Nishikawa M., Yuto S., Hasegawa T., Shiroishi W., Honghao H., Nakabayashi Y., Nosaka Y., Saito N. Compositing effects of $CuBi_2O_4$ on visible-light responsive photocatalysts. *Mater. Sci. Semicon. Proc*, 2017, vol. 57, pp.12–17. doi: 10.1016/j.mssp.2016.09.013.

17 Zhu, L.; Basnet, P.; Larson, S. R.; Jones, L. P.; Howe, J. Y.; Tripp, R. A.; Zhao, Y. Visible Light-Induced Photoeletrochemical and Antimicrobial Properties of Hierarchical $CuBi_2O_4$ by Facile Hydrothermal Synthesis. *Chemistry Select*, 2016, no. 1, pp. 1518-1524.

18 Sharma, G.; Zhao, Z.; Sarker, P.; Nail, B. A.; Wang, J.; Huda, M. N.; Osterloh, F. E. Electronic structure, photovoltage, and photocatalytic hydrogen evolution with p- $CuBi_2O_4$ nanocrystals. *J. Mater. Chem. A*, 2016, no. 4, pp. 2936-2942.

19 Fuxian Wang. (2017) *Multinary Metal Oxides for Solar Water Splitting: Towards High Efficiency and High Stability*. Doctoral Thesis in Inorganic chemistry. Berlin, https://depositonce.tu-berlin.de//handle/11303/7307 10.14279/depositonce-6580

20 Donghyeon Kang, James C. Hill, Yiseul Park, Kyoung-Shin Choi. Photoelectrochemical Properties and Photostabilities of High Surface Area $CuBi_2O_4$ and Ag-Doped $CuBi_2O_4$ Photocathodes. *Chemistry of Materials*, 2016, vol. 28, no. 12, pp. 4331-4340. doi:10.1021/acs.chemmater.6b01294.

21 Nakabayashi Y., Nishikawa M., Saito N. Relationship between the morphology for the photo-electrode of copper bismuth oxide and the photo-electrochemical activity related to water reduction. *J. Chem. Sci*., 2021, 133:12 https://doi.org/10.1007/s12039-020-01876-0

22 Chang-Ming Jiang, Gideon Segev, Lucas H. Hess, Guiji Liu, Gregory Zaborski, Francesca M. Toma, Jason K. Cooper, Ian D. Sharp. Understanding Energy Conversion and Loss Mechanisms in Ternary Metal Oxide Photoelectrodes: The Case of Copper Vanadate. *Materials Science*, 2017, 1. doi: 10.26434/chemrxiv.5514871.v1.