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Influence of temperature on quantum efficiency of photo-electrochemical water splitting by metal—semiconductor micro- and nanodendrites

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The internal quantum efficiency of photo-catalytic splitting of water, similar in composition with sea water, and the influence of temperature on photo-catalytic processes were studied. It was shown that maximum quantum efficiency at room temperature for Ag—AgI photocathodes is 1.9% and for Cu—CuI photocathodes is 1.2%. The efficiency increases exponentially with temperature rise.

Keywords: silver, copper iodide, sea water, photo catalyze, water splitting.

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Photocathodes based on porous metal layers are of interest for photoelectrochemical decomposition of water into hydrogen and oxygen in the solar power engineering. Some papers show the capabilities for effective decomposition of water in nanoporous layers of metals and semiconductors [1–7].

The experiments of photoelectrochemical decomposition of water mainly use electrolytes not related to the chemical composition of natural water. However, for the practical applications, it is important to study the efficacy of photocatalytic (PC) decomposition of natural, in particular, sea water. Under PC-decomposition of natural water its temperature may change depending on the time of the year and the day. Therefore, the important objective is to also study the impact of water temperature at quantum efficiency (QE) of its PC-decomposition. The objective of this paper is to study the impact of temperature at QE of water decomposition by photoelectrochemical method in the electrolyte with the composition similar to that of sea water.

The base for the photocathodes with nanostructured (NS) layers of silver, copper and their iodides were the polished copper and iron plates. For synthesis of NS-layers from silver and copper, chemical reactions of substitution were used [8]. For synthesis of NS-layer of silver, copper substrates were submerged into aqueous solution $AgNO_3$ (3.75 wt.%). For synthesis of NS-layers of copper, iron substrates were submerged into aqueous solution $CuSO_4 \cdot 5H_2O$ (5 wt.%). Reaction duration was 4 s. For iodination, the produced NS-layers of silver and copper were placed into a tank with saturated iodine vapors. Iodination was carried out at room temperature for 10—30 min.

For PC-decomposition of water, the photocathode was placed into a cell filled with „sea" water and was illuminated through a window of quartz glass. To imitate sea water, aqueous solution of NaCl (77.8), $MgCl_2$ (10.9), $MgSO_4$ (4.7), KCl (2.5), K_2SO_4 (2.5) mix was used. The brackets contain the mass fraction percentage.

The source of light was Novacure 2100 c light with mercury lap of 3 W capacity and spectral interval of radiation 250—500 nm. The PC-cell was exposed to DC voltage $U = 0.5-5\,\mathrm{V}$ through a ballast resistor 1 kΩ. The inner QE of photocatalysis was determined using the method described in [9].

Analysis of the images produced using a scanning electron microscope showed that NS-layers were branching nanostructures in the form of fractal dendrites with length of 20 nm—3 μm (fig. 1). Increase of the effective area of NS-layer relative to the substrate surface area exceeds 10^4 times. If the synthesis conditions are complied with. the coefficient of photocathode effective surface area increase is maintained.

When the photocathode of NS-iodide of silver or copper is placed into a PC-cell filled with electrolyte, and light flux is supplied to the photocathode, photocurrent appears in the cell. This indicates release of electrons from the photocathode and the photoelectrochemical reaction.

QE dependences on voltage in the PC-cell for photocathodes from Ag—AgI and Cu—CuI are shown in fig. 2. From the figure you can see that as voltage increases, the PC-cell shows QE growth, and at $U > 3\,\mathrm{V}$ the dependence is saturated. Maximum QE of decomposition for the „sea" water for the photocathode from Ag—AgI is 1.9 %. Maximum QE of decomposition in case of the photocathode of Cu—CuI is 1.2 %. The reason for this may be the fact that the plasma wavelength of Ag is 390 nm, and the plasma wavelength of Cu is 550 nm. Therefore, the surface plasmons in Ag are excited in a wider spectral interval.

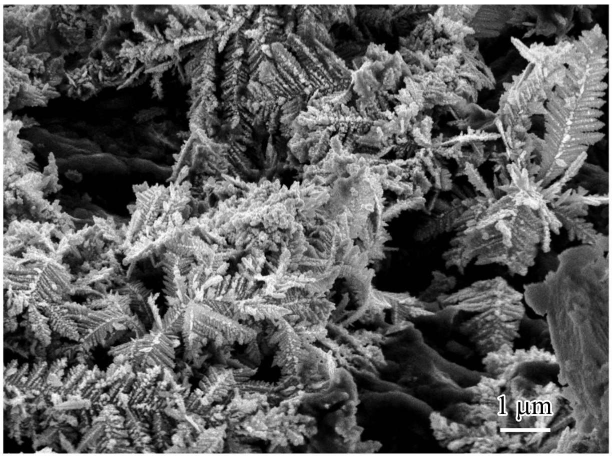

Figure 1. Image of Ag−AgI photocathode surface made with a scanning electron microscope.

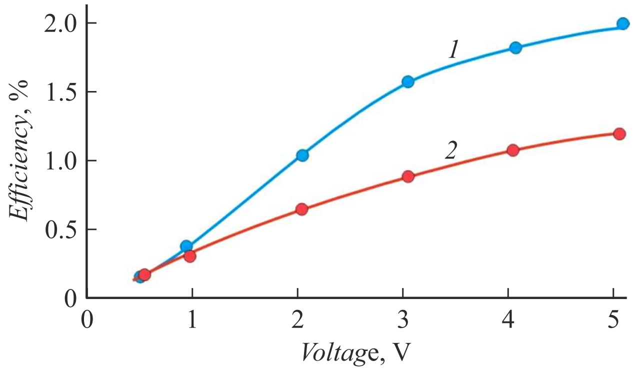

Figure 2. Dependence of water FC-decomposition QE on voltage for nanoporous layer from Ag−AgI (*1*) and Cu−CuI (*2*) after partial iodination. $T = 20\,^\circ$C.

Temperature dependences of water PC-decomposition QE for photocathodes of Ag−AgI and Cu−CuI are shown in fig. 3. From the figure you can see that the dependences are close to the exponent. Dependences for the photocathode from Ag−AgI with „the sea“ water are steeper than in the case of the photocathode from Cu−CuI. If the synthesis conditions are maintained, the dependences shown in fig. 2 and 3, are maintained within 5 % when photocathodes of various types are used.

In case of surface photoeffect the electron absorbs the photon energy at the interface, and it may exit the metal with low energy losses. The electron after its exit into electrolyte may reduce the hydrogen ions. In case of fractal metal dendrites with the developed surface, the surface photoeffect makes it possible to increase the PC-decomposition QE. For the partial iodination of silver and copper dendrites, the presence of metal−semiconductor interface causes the reduction of the potential barrier for the exit of photoelectrons from metal to semiconductor and further into electrolyte.

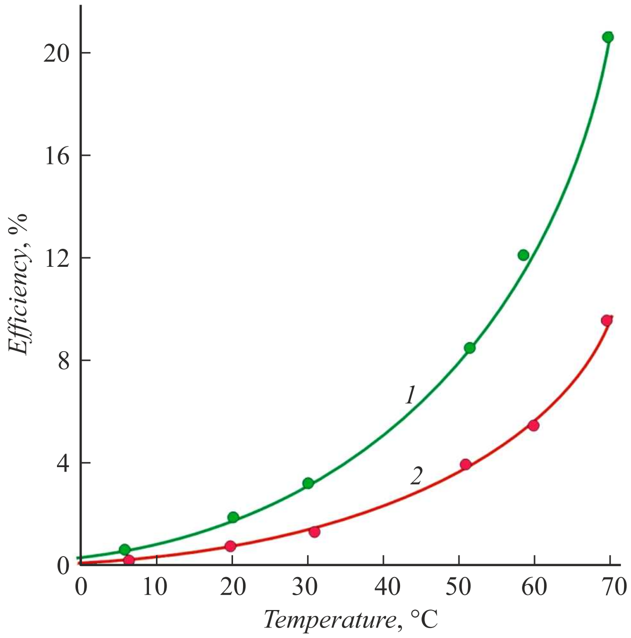

Figure 3. Temperature dependence of QE of water PC-decomposition for the photocathode from Ag−AgI (*1*) and Cu−CuI (*2*). $U = 3$ V.

Let us consider the contribution of electrolyte heating to PC-decomposition processes. The electrolyte heating processes may be related to macro- and microeffects. In the first case the entire volume of electrolyte is heated. In the second case — only the thin layer of electrolyte near the photocathode. Besides, in „the hot points“ due-to increased intensity of the electromagnetic wave, the local heating of electrolyte happens at nanoscale. Strong heating of electrolyte at nanoscale may cause local intensification of cavitation and micro- and nanobubbles of gas. Ion conductance, according to the Arrhenius law, grows exponentially with temperature growth. Specific electric conductivity of electrolytes increases as the electrolyte temperature increases (Kohlrausch effect). Heating of the semiconductor layer also causes higher QE of water decomposition due to increase of its conductance and decrease of the band gap width. Therefore, the local heating of electrolyte causes increase in the water decomposition QE.

Therefore, the temperature dependence of QE of „the sea“ water decomposition is close to the exponential one, and at $T = 70\,^\circ$C QE may reach 20 %. The causes for this are both the photocathode heating with radiation and local heating of electrolyte near the photocathode surface.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] C.G. Morales-Guio, S.D. Tilley, H. Vrubel, M. Grätzel, X. Hu, Nat. Commun., **5**, 3059 (2014). DOI: 10.1038/ncomms4059

[2] M.G. Walter, E.L. Warren, J.R. McKone, S.W. Boettcher, Q. Mi, E.A. Santori, N.S. Lewi, Chem. Rev., **110**, 6446 (2010). DOI: 10.1021/cr1002326

[3] Y. Ben-Shahar, F. Scotognella, I. Kriegel, L. Moretti, G. Cerullo, E. Rabani, U. Banin, Nat. Commun., **7**, 10413 (2016). DOI: 10.1038/ncomms10413

[4] J. Gan, X. Lu, Y. Ton, Nanoscale, **6**, 7142 (2014). DOI: 10.1039/c4nr01181c

[5] A.N. Koya, X. Zhu, N. Ohannesian, A.A. Yanik, A. Alabastri, R.P. Zaccaria, R.K.W.-C. Shih, D. Garoli, ACS Nano, **5**, 6038 (2021). DOI: 10.1021/acsnano.0c10945

[6] A.N. Koya, J. Cunha, T.-L. Guo, A. Toma, D. Garoli, T. Wang, S. Juodkazis, D. Cojoc, R.P. Zaccaria, Adv. Opt. Mater., **8**, 1901481 (2020). DOI: 10.1002/adom.201901481

[7] T.V. Blank, Yu.A. Gol'dberg, Semicomductors, **41** (11), 1263 (2007). DOI: 10.1134/S1063782607110012.

[8] P.A. Bezrukov, A.V. Nashchekin, N.V. Nikonorov, A.I. Sidorov, Phys. Solid State, **64** (8), 1081 (2022). DOI: 10.61011/0000000000.

[9] R. Ron, E. Haleva, A. Salomon, Adv. Mater., **30**, 1706755 (2018). DOI: 10.1002/adma.201706755

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