Effective $p$-type photocurrent sensitization of $n$-Bi$_2$O$_3$ with $p$-CuBi$_2$O$_4$ and $p$-CuO: Z-scheme photoelectrochemical system

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Received: 17 September 2019 / Revised: 3 January 2020 / Accepted: 3 January 2020 / Published online: 15 January 2020
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Abstract
Nanostructured $n$-Bi$_2$O$_3/p$-CuBi$_2$O$_4/p$-CuO photocathodes with incident photon-to-current conversion efficiency IPCE$_{\text{max}}$ = 70% ($\lambda$ = 400 nm) have been prepared using electrochemical and chemical methods. Platelet-like BiOI nanocrystals electrochemically deposited on FTO substrate were used as precursors. CuI nanoparticles were deposited on the BiOI surface by successive ionic layer adsorption and reaction technique. Oxidative heat treatment of BiOI/CuI heterostructure in air leads to the formation of the Bi$_2$O$_3$/CuBi$_2$O$_4$/CuO composite. Binary oxide was formed as a result of solid-state interaction between bismuth and copper oxides at their interface.

Spectral sensitization of wide-gap $n$-Bi$_2$O$_3$ (band gap $E_g$ = 2.80 eV) with narrow-gap $p$-CuBi$_2$O$_4$ ($E_g$ = 1.80 eV) and $p$-CuO ($E_g$ = 1.45 eV) extends spectral sensitivity range up to 800 nm by Z-scheme implementation: cathodic photocurrent is associated with the transition of photoelectrons from $p$-CuBi$_2$O$_4$ and $p$-CuO to the solution, while photoholes recombine with electrons of $n$-Bi$_2$O$_3$ conduction band. High quantum efficiency of photocurrent was achieved due to band-edge correlation in a three-component oxide heterostructure, combined with an internal electric field in $p$-CuBi$_2$O$_4$ and effective photon absorption by two narrow-band-gap $p$-CuBi$_2$O$_4$ and $p$-CuO semiconductors.

Keywords Photoelectrochemistry · CuBi$_2$O$_4$ · Photocurrent sensitization · Water splitting · Solar cells

Introduction
The possibility of using binary copper(II) and bismuth(III) oxide CuBi$_2$O$_4$ as a photocathode for photoelectrolysis of water was first shown in [1]. This oxide semiconductor has a hole-type conductivity and a relatively small band gap $E_g$ = 1.80 eV [2] allowing to use a significant part of solar spectrum. Further studies had shown that $p$-CuBi$_2$O$_4$ is characterized by an extremely positive flat band potential (1.26–1.43 V vs RHE [3]). It indicates a thermodynamically favorable location of its conduction band edge with respect to the electrode potential of H$_2$O/H$_2$ system. The rate of photoelectrochemical hydrogen evolution on $p$-CuBi$_2$O$_4$ surface (the value of the cathodic photocurrent) can be increased by the deposition of catalysts, for example, highly dispersed platinum [4].

At the same time, low values of carrier mobility ($1.2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$), lifetime (32–819 ns), and diffusion length (10–52 nm) significantly limit the magnitude of cathodic photocurrent—up to 0.5 mA cm$^{-2}$ at 0.4 V vs RHE for optimized CuBi$_2$O$_4$/Pt photocathodes under AM 1.5 illumination [4]. Simple decrease of CuBi$_2$O$_4$ crystallite size is not the
optimal solution to problems of charge transport and recombination reduction, since photoholes need to achieve a conductive FTO substrate and overcome many intercrystalline boundaries. The authors of [4] suggested that the promising ways to increase the quantum efficiency of photocurrent are deposition of CuB\textsubscript{2}O\textsubscript{4} nanocrystals on conductive substance (for example, graphene), as well as bulk doping of a binary oxide to increase the conductivity.

The doping was successfully implemented for p-CuB\textsubscript{2}O\textsubscript{4} by creation of copper concentration gradient. Decrease of Cu/Bi ratio in CuB\textsubscript{2}O\textsubscript{4} photocathodes introduces Cu vacancies that increase the carrier (hole) concentration and lowers the Fermi level. At the same time, the flat band potential shifts towards more positive potentials. Thus, a gradient in Cu vacancies leads to an internal electric field within CuB\textsubscript{2}O\textsubscript{4}, which can facilitate charge separation [5].

Doping of p-CuB\textsubscript{2}O\textsubscript{4} with Ag\textsuperscript{+} ions also leads to an increase of cathodic photocurrent and contributes to an increase of photocorrosion stability of the electrodes [6]. One of the reasons for this effect is associated with an increase in the concentration of majority current carriers in the semiconductor (holes) as a result of the replacement of Bi\textsuperscript{3+} with Ag\textsuperscript{+} ions.

The most well-known and a fairly simple method for CuB\textsubscript{2}O\textsubscript{4} preparation is a high-temperature synthesis from individual oxides [7]. It is possible to use aqueous solutions of bismuth(III) and copper(II) nitrates, which are applied to hot substrates. The oxidative heat treatment of BiOI/CuI composite electrode, but also to provide a necessary band-edge correlation in heterojunction.

Experimental

Electrodeposition of BiOI on FTO substrate from a solution of 0.1 mol dm\textsuperscript{-3} Bi(NO\textsubscript{3})\textsubscript{3} + 1 mol dm\textsuperscript{-3} KI was carried out according to the technique described in [9, 10]. The solution was acidified to pH 1.93 with dilute nitric acid. Then, benzoquinone was added to the solution (0.1 mol dm\textsuperscript{-3}).

Electrochemical formation of BiOI layers was carried out at a potential of −100 mV for 100 s. Then, the deposition process was repeated again in the same electrolyte at a temperature of 70 °C to obtain a thicker film (up to 2 μm thick).

Cul was deposited on BiOI surface by SILAR method by alternately immersing FTO/BiOI electrode into 0.1 mol dm\textsuperscript{-3} KI solution, distilled water, saturated Cu(NO\textsubscript{3})\textsubscript{2} solution, and distilled water (one deposition cycle). The electrode was immersed into the solutions for 30 s under vigorous stirring with a magnetic stirrer. The number of Cul deposition cycles varied from 50 to 200.

Electrochemical measurements were carried out in a standard three-electrode cell with a volume of 50 ml with a Pt auxiliary electrode and a saturated silver chloride reference electrode Ag | AgCl | KCl\textsubscript{sat} (+0.201 V relative to the standard hydrogen electrode). All electrode potentials are presented with respect to this reference electrode. Electrochemical (PEC) measurements were performed in 0.1 mol dm\textsuperscript{-3} Na\textsubscript{2}HPO\textsubscript{4} + 0.1 mol dm\textsuperscript{-3} NaH\textsubscript{2}PO\textsubscript{4} (pH 6.7) + 0.3 mol dm\textsuperscript{-3} Na\textsubscript{2}SO\textsubscript{4} aqueous solution with the addition of 10 mmol dm\textsuperscript{-3} H\textsubscript{2}O\textsubscript{2}. Working electrode was illuminated from a solution side by a LED with 465 nm wavelength and 1 mW cm\textsuperscript{-2} light intensity.

Photocurrent spectra were obtained using a setup equipped with a high-intensity grating monochromator (spectral resolution 1 nm), a 250-W halogen lamp, and a light chopper. The spectral dependences of the incident photon-to-current conversion efficiency (IPCE) were calculated from the photocurrent spectra and light intensity distribution at the monochromator output [11].

Scanning electron microscopy (SEM) and EDS element mapping was performed using dual beam system Helios Nanolab 650 (FEI) with the X-Max 20 X-ray detector and Inca EDX software (Oxford Instruments). X-ray diffraction (XRD) analysis was performed using Bruker D8 Advance
diffractometer (Bragg-Brentano geometry, Cu Kα emission, 0.5° min⁻¹).

Raman spectra were measured at room temperature using a Nanofinder HE confocal spectrometer (LOTIS TII, Belarus-Japan) with a 532-nm solid-state CW laser as the excitation source. Incident optical power was 60 µW. Backscattered light without analysis of its polarization was dispersed with a spectral resolution of 2.5 cm⁻¹ (0.1 nm) and detected with a cooled CCD-matrix. Signal acquisition time was equal to 60 s. The excitation spot diameter was about 1 µm. Spectral calibration was done using a built-in gas-discharge lamp providing accuracy better than 2.5 cm⁻¹ (0.1 nm) [11].

Results and discussion

SEM, XRD, and Raman characterization of n-Bi₂O₃/p-CuBi₂O₄/p-CuO

Electrodeposited BiOI is composed of randomly located platelet-like crystallites with a thickness of 30–40 nm with lateral dimension of 1–2 µm and mostly perpendicular orientation to the surface (Fig. 1a). Such structure is typical for BiOI films prepared by various chemical and electrochemical methods [9, 10]. Heating of BiOI film in air at 450 °C for 2 h leads to the formation of bismuth oxide. Complete oxidation of BiOI with the formation of the polymorphic α-Bi₂O₃ modification is confirmed by X-ray diffraction analysis (Fig. 2a). Morphology of Bi₂O₃ film obtained after heating repeats the initial platelet-like structure of BiOI precursor film (Fig. 1b). The average size of Bi₂O₃ crystallites determined from the Debye-Scherrer equation is 36 nm. The oxide particles are lined up in such a way that the microstructure of BiOI precursor is repeated.

Immersion of BiOI film in Cu(NO₃)₂ solution is accompanied by Cu²⁺ ion adsorption and their interaction with I⁻ ions during subsequent immersion in KI solution:

\[ 2\text{Cu}^{2+} + 5\text{I}^- \rightarrow 2\text{CuI} \downarrow + \text{I}_3 \]

It should be noted that the deposition of CuI on BiOI surface does not change the microstructure of BiOI plate crystallites (Fig. S1). CuI nanoparticles formed on BiOI surface were identified by X-ray analysis (Fig. S2).

Thermal treatment of BiOI/CuI heterostructure in air at 450 °C leads to the oxidative transformation of BiOI and

![Fig. 1 SEM images of surface of BiOI (a), Bi₂O₃ (b), and Bi₂O₃/CuBi₂O₄/CuO (c, d). The number of CuI deposition cycles, 50 (c) and 150 (d)](image)

![Fig. 2 XRD patterns of Bi₂O₃ (a) and Bi₂O₃/CuBi₂O₄/CuO (b, c). The number of CuI SILAR deposition cycles N = 100 (b) and 200 (c)](image)
Cul into bismuth and copper oxides:

\[
\begin{align*}
4\text{BiOI} + \text{O}_2 & \rightarrow 2\text{Bi}_2\text{O}_3 + 2\text{I}_2, \\
2\text{CuI} + \text{O}_2 & \rightarrow 2\text{CuO} + \text{I}_2.
\end{align*}
\]

Solid-state reaction between the oxides leads to the formation of a composite oxide at the Bi\(_2\)O\(_3\)/CuO heterointerface:

\[
\text{Bi}_2\text{O}_3 + \text{CuO} \rightarrow \text{CuBi}_2\text{O}_4.
\]

After the thermal treatment of BiOI/CuI heterostructure in air at 450 °C, the initial platelet-like structure of BiOI film had undergone a significant transformation and roundish particles of non-uniform shape were formed (Fig. 1c, d). The formation of three oxide phases Bi\(_2\)O\(_3\), CuBi\(_2\)O\(_4\), and CuO is confirmed by the XRD analysis (Fig. 2b, c). Since bismuth oxide is formed from BiOI, which is present on the electrode surface in considerable excess with respect to CuI, the most intense reflexes belong to BiOI. Estimation of crystallite sizes from the Debye-Scherrer equation indicates that the crystallite sizes of all three oxides (Bi\(_2\)O\(_3\), CuBi\(_2\)O\(_4\), and CuO) are of the same order of magnitude and equals to several tens of nm (Table 1).

As noted above, the amount of CuBi\(_2\)O\(_4\) and CuO in Bi\(_2\)O\(_3\)/CuBi\(_2\)O\(_4\)/CuO composite was varied by changing the number of CuI precursor SILAR deposition cycles (N). The crystallite size of the oxides has a certain tendency to increase with increasing N (Table 1).

The formation of Bi\(_2\)O\(_3\), CuBi\(_2\)O\(_4\), and CuO was confirmed by Raman spectroscopy. In Raman spectra of individual Bi\(_2\)O\(_3\), peaks corresponding to α-Bi\(_2\)O\(_3\) are observed at 92 cm\(^{-1}\), 126 cm\(^{-1}\), 185 cm\(^{-1}\), 307 cm\(^{-1}\), 333 cm\(^{-1}\), 471 cm\(^{-1}\), and also overtones at 600 cm\(^{-1}\) [12] (Fig. 3a). Formation of CuBi\(_2\)O\(_4\) is accompanied by the appearance of several intense peaks in the Raman spectra, including the most intense peak at 131 cm\(^{-1}\) and its overtones at 260 cm\(^{-1}\) and 400 cm\(^{-1}\) [13–16]. The peak at ~290 cm\(^{-1}\) and weak broad band in the region of 1100–1200 cm\(^{-1}\) are associated with CuO (Fig. 3b–d) [17].

Thus, the X-ray diffraction analysis and Raman spectroscopy indicate that the heat treatment of BiOI/Cul heterostructure in air leads to the formation of Bi\(_2\)O\(_3\)/CuBi\(_2\)O\(_4\)/CuO oxide heterostructure. General scheme of Bi\(_2\)O\(_3\)/CuBi\(_2\)O\(_4\)/CuO synthesis is shown in Fig. 4.

### Photoelectrochemical properties of n-Bi\(_2\)O\(_3\)/p-CuBi\(_2\)O\(_4\)/p-CuO heterostructure

Bi\(_2\)O\(_3\) oxide belongs to wide-gap semiconductors (\(E_g = 2.80\) eV [18]) and is capable to generate anodic photocurrent under illumination with photon energy exceeding the band gap (Fig. 5, curve 1). Anodic photocurrent onset potential \(E_{on}\) is +0.15 V. As is well known, such PEC behavior is typical for n-type semiconductors. The maximum quantum efficiency of photocurrent for Bi\(_2\)O\(_3\) was small and did not exceed 2%. This photocurrent is contributed to the following redox processes:

### Table 1 Dimensions of crystallites in Bi\(_2\)O\(_3\) and Bi\(_2\)O\(_3\)/CuBi\(_2\)O\(_4\)/CuO films determined from X-ray diffraction patterns

| Sample                  | Bi\(_2\)O\(_3\) crystallites average size (nm) | CuO crystallites average size (nm) | CuBi\(_2\)O\(_4\) crystallites average size (nm) |
|-------------------------|-----------------------------------------------|-----------------------------------|-----------------------------------------------|
| Bi\(_2\)O\(_3\)         | 36                                            | –                                 | –                                             |
| Bi\(_2\)O\(_3\)/CuBi\(_2\)O\(_4\)/CuO (N = 100) | 34                                            | 21                                | 23                                            |
| Bi\(_2\)O\(_3\)/CuBi\(_2\)O\(_4\)/CuO (N = 200) | 38                                            | 36                                | 46                                            |
H$_2$O$_2$–2e$^-$ = O$_2$ + 2H$^+$  \( E^0 = 0.68 \) V (vs. SHE),
2H$_2$O– 4e$^-$ = O$_2$ + 4H$^+$  \( E^0 = 1.23 \) V (vs.SHE).

Hydrogen peroxide oxidation is more preferable from a thermodynamic point of view than oxidation of water. Formation of \( p\)-CuBi$_2$O$_4$ and \( p\)-CuO particles with hole-type conductivity at the surface of \( n\)-Bi$_2$O$_3$ dramatically changes the situation—cathodic photocurrent starts at \( E_{on} = 0.50 \) V and becomes dominant (Fig. 5, curve 2). The dark current is negligible up to a potential of \(-0.2 \) V. Photocurrent increases with the increase of cathodic polarization of the electrode.

It should be noted that photoelectrochemical measurements were carried out in phosphate buffer containing H$_2$O$_2$ as an effective acceptor of photoelectrons. Such solution was used in the previous study of individual \( p\)-CuBi$_2$O$_4$ films \[4\]. Therefore, the following reaction corresponds to the cathodic photocurrent:

\[
\text{H}_2\text{O}_2 + 2\text{e}^- = 2\text{OH}^- 
\]

The reduction of H$_2$O$_2$ minimizes the recombination losses of photo charges at the electrode/electrolyte interface and increases photocorrosion resistance of \( p\)-CuBi$_2$O$_4$ \[4\]. The use of identical solutions makes it possible to compare the photocurrent values of the composite \( n\)-Bi$_2$O$_3$/\( p\)-CuBi$_2$O$_4$/\( p\)-CuO photoelectrode and an individual \( p\)-CuBi$_2$O$_4$ film.

Spectral dependences of IPCE are presented on Fig. 6a. The maximum values of photocurrent quantum efficiency reach more than 70% in the shortwave region of spectrum (\( \lambda < 400 \) nm). Since \( p\)-CuBi$_2$O$_4$ and \( p\)-CuO semiconductors have a band gap of 1.80 eV and 1.45 eV, respectively, they are capable of absorbing photons in the visible spectral region.

The main photon absorption and photocharge generation occur in these two narrow-band components of the heterojunction, namely in \( p\)-CuBi$_2$O$_4$ and \( p\)-CuO, because bismuth oxide does not absorb light with \( \lambda > 440 \) nm. The IPCE values of the electrodes exceed from 1.17 times to more than an order magnitude previously achieved for an individual \( p\)-CuBi$_2$O$_4$ film and heterostructures based on it (Table 2).

What are the reasons for an extremely high PEC activity of \( n\)-Bi$_2$O$_3$/\( p\)-CuBi$_2$O$_4$/\( p\)-CuO heterostructure? Let us consider the energy diagram presented in Fig. 7. Since bismuth oxide does not absorb radiation with \( \lambda > 440 \) nm, the main photon absorption and photocharge generation occur in two narrow-band components of the heterojunction namely in \( p\)-CuBi$_2$O$_4$ and \( p\)-CuO. As shown above (see Fig. 5), cathodic photocurrent \( E_{on} \) of \( p\)-CuBi$_2$O$_4$ and \( p\)-CuO is more positive than the \( E_{on} \) value for \( n\)-Bi$_2$O$_3$. Thus, on the energy scale, the conduction band edge of bismuth oxide is higher than the valence band edge of oxides with hole-type conductivity. Since the conduction band edge of CuBi$_2$O$_4$ has a higher energy than the conduction band edge of CuO (Fig. 7), it makes...
possible photoelectron transfer from CuBi$_2$O$_4$ to CuO and further to the solution.

During cathodic photocurrent generation, photoelectrons are captured by electrolyte components, primarily by hydrogen peroxide, and the holes are transported towards Bi$_2$O$_3$ and recombine with $n$-Bi$_2$O$_3$ conduction band electrons. Concentration of electrons in the conduction band of $n$-type bismuth oxide can be sufficiently high, up to $10^{18}$–$10^{20}$ cm$^{-3}$ [19, 20] due to ionization of donor defects. Therefore, in the composite electrode $n$-Bi$_2$O$_3$/p-CuBi$_2$O$_4$/p-CuO, the spatial separation of charges occurs according to the so-called Z-scheme [21], i.e., by recombination of photoholes from p-CuBi$_2$O$_4$ and p-CuO with dark electrons in $n$-Bi$_2$O$_3$ (Fig. 7). The transport of photoholes to the heterointerface seems unlikely, since in this case, the anodic photocurrent will be observed.

In work [5], it was shown that $p$-CuBi$_2$O$_4$ with gradient doping over the film thickness can be obtained in a rather simple way—by layer-by-layer deposition of Bi$_2$O$_3$ and CuO oxides on FTO substrate with subsequent thermal treatment. The highest concentration of acceptor centers (copper cation $V_{Cu}^{2+}$ vacancies) is observed in CuBi$_2$O$_4$ layer adjacent to the interface with FTO. In our case, CuO phase also forms on Bi$_2$O$_3$ surface with subsequent formation of binary CuBi$_2$O$_4$ oxide. However, we have a large excess of Bi$_2$O$_3$ precursor, and CuO do not completely convert into CuBi$_2$O$_4$. Gradient distribution of Cu throughout the Bi$_2$O$_3$/CuBi$_2$O$_4$/CuO film was proved by element mapping (Fig. S4). It can be presumed that in our case, the gradient distribution of $V_{Cu}^{2+}$ in CuBi$_2$O$_4$ also takes place creating an internal field; in Fig. 7, it is reflected by the slope of the energy bands, contributing the drift of photoholes in Bi$_2$O$_3$ and their spatial separation with photoelectrons. Photoelectrons in CuBi$_2$O$_4$, in turn, due to the higher position of CuBi$_2$O$_4$ conduction band edge as compared with CuO conduction band edge, are transported to interface with electrolyte.

**Table 2** IPCE values for different CuBi$_2$O$_4$ electrodes

| Electrode | IPCE at $\lambda = 400$ nm (%) | Solution, electrode potential ($E$) | Reference |
|-----------|-------------------------------|-----------------------------------|-----------|
| $p$-CuBi$_2$O$_4$ | ~28 | 0.1 M Na$_2$HPO$_4$ + 0.1 M NaH$_2$PO$_4$ (pH 6.7) + 0.3 M K$_2$SO$_4$ + 10 mM H$_2$O$_2$ $E = +0.6$ V (RHE) | [4] |
| $p$-CuBi$_2$O$_4$ (gradient self-doped) | ~60 | 0.1 M Na$_2$HPO$_4$ + 0.1 M NaH$_2$PO$_4$ (pH 6.7) + 0.3 M K$_2$SO$_4$ + 10 mM H$_2$O$_2$ $E = +0.6$ V (RHE) | [5] |
| Ag-doped $p$-CuBi$_2$O$_4$ | ~8 | 0.1 M NaOH saturated with O$_2$ $E = +0.6$ V (RHE) | [6] |
| $p$-CuBi$_2$O$_4$ | ~0.9 | 0.5 M NaHCO$_3$ saturated with CO$_2$ $E = -0.3$ V (Ag/AgCl/3 M KCl) | [8] |
| $n$-Bi$_2$O$_3/p$-CuBi$_2$O$_4$ | ~0.1 | 0.5 M NaHCO$_3$ saturated with CO$_2$ $E = -0.3$ V (Ag/AgCl/3 M KCl) | [8] |
| $p$-CuO/$p$-CuBi$_2$O$_4$ | ~4.5 | 0.5 M NaHCO$_3$ saturated with CO$_2$ $E = -0.3$ V (Ag/AgCl/3 M KCl) | [8] |
| $n$-Bi$_2$O$_3/p$-CuBi$_2$O$_4/p$-CuO ($N = 150$) | ~70 | 0.1 M Na$_2$HPO$_4$ + 0.1 M NaH$_2$PO$_4$ (pH 6.7) + 0.3 M Na$_2$SO$_4$ + 10 mM H$_2$O$_2$ $E = -0.2$ V (Ag/AgCl/KCl sat) | This work |
As can be seen from Fig. 6b, the IPCE value tends to increase with the increasing number of SILAR cycles \( N \) and accordingly with an increase of the amount of CuBi\(_2\)O\(_4\) and CuO. These \( p \)-type components of the heterostructure act as a photosensitizer of the PEC process. For \( \lambda = 400 \) nm (Fig. 6b, curve 1) and \( \lambda = 440 \) nm (Fig. 6b, curve 2), the IPCE–\( N \) dependence passes through a maximum. Similar dependences were observed when CdS nanoparticles were deposited on oxide semiconductors: TiO\(_2\), ZnO, and In\(_2\)O\(_3\) [22]. The presence of maximum is due to the fact that with an increase in the thickness of the sensitizer layer, photoelectrons need to overcome a greater distance and, accordingly, a greater number of intercrystalline boundaries where recombination occurs [22]. A similar situation is observed in our case for \( n \)-Bi\(_2\)O\(_3\)/\( p \)-CuBi\(_2\)O\(_4\)/\( p \)-CuO heterostructure. With the increase in the wavelength of light, its absorption depth in CuBi\(_2\)O\(_4\) and CuO increases and photoholes need to pass a shorter distance to reach the FTO surface. As a result, the maximum on the IPCE–\( N \) dependences gradually shifts towards larger \( N \) with increasing \( \lambda \), and, accordingly, the light absorption depth. At \( \lambda = 550 \) nm, maximum disappears and photocurrent increases continuously with an increase of sensitizer amount (Fig. 6b, curve 4).

By analogy with the previously demonstrated increase in photocurrent by deposition of electrocatalytic particles on semiconductor photoelectrodes [23–26], photocurrent values on \( n \)-Bi\(_2\)O\(_3\)/\( p \)-CuBi\(_2\)O\(_4\)/\( p \)-CuO heterostructure can be increased due to the deposition of highly dispersed platinum. Platinum nanoparticles were deposited by dip coating [27] of \( n \)-Bi\(_2\)O\(_3\)/\( p \)-CuBi\(_2\)O\(_4\)/\( p \)-CuO electrode in H\(_2\)PtCl\(_6\) (5 mmol dm\(^{-3}\)) followed by drying at 60 °C and heating in air at 450 °C for 1 h. The formation of platinum nanoparticles on the electrode surface was confirmed by XRD patterns (Fig. S3).

Deposition of platinum nanoparticles on \( n \)-Bi\(_2\)O\(_3\)/\( p \)-CuBi\(_2\)O\(_4\)/\( p \)-CuO surface leads to an increase of IPCE by 10%. At the same time, the potential of the photocurrent onset and the long-wave edge of spectral sensitivity of remains almost unperturbed. Thus, surface modification of \( n \)-Bi\(_2\)O\(_3\)/\( p \)-CuBi\(_2\)O\(_4\)/\( p \)-CuO with Pt nanoparticles can be considered an effective method for increasing the photoelectrochemical activity of photocathode.

**Conclusions**

In this study, a new method of preparation of \( n \)-Bi\(_2\)O\(_3\)/\( p \)-CuBi\(_2\)O\(_4\)/\( p \)-CuO nanoheterostructure by electrochemical deposition of BiOI on FTO substrate with subsequent deposition of copper(I) iodide and oxidative thermal treatment of the resulting BiOI/Cul film in air at 450 °C has been proposed. Thermal treatment of BiOI/Cul heterostructure in air leads to the formation of not only individual bismuth and copper
oxides but also binary CuBi$_2$O$_4$ oxide due to solid-state interaction between Bi$_2$O$_3$ and CuO.

The extension of the spectral range of photocurrent generation up to 800 nm is due to the spectral sensitization of wide band-gap n-Bi$_2$O$_3$ substrate ($E_g = 2.80$ eV) by narrow-gap p-CuBi$_2$O$_4$ ($E_g = 1.80$ eV) and p-CuO ($E_g = 1.45$ eV). This process can be considered in the framework of the Z-scheme including cathodic photocurrent generation by photoelectron transfer from p-CuBi$_2$O$_4$ and p-CuO to the electrolyte and photohole recombination with electrons from n-Bi$_2$O$_3$ conduction band.

High photocurrent quantum efficiency (IPCE = 70% at $\lambda = 400$ nm) is achieved due to the band-edge correlation in three-component oxide heterostructure, and effective absorption of light by two narrow-band semiconductors p-CuBi$_2$O$_4$ and p-CuO, and, probably, because of the presence of internal field in p-CuBi$_2$O$_4$. The value of IPCE strongly depends on the amount of p-CuBi$_2$O$_4$ and p-CuO sensitizers, which was varied by changing the number of SILAR cycles. Photocurrent quantum efficiency in shortwave spectral region ($\lambda < 500$ nm) passes through a maximum with increasing N, while at $\lambda \sim 550$ nm, photocurrent continuously increases with increasing amount of p-CuBi$_2$O$_4$ and p-CuO. The maximum IPCE values can be increased from 70 to 80% by depositing highly dispersed platinum on the electrode surface. The high photocurrent quantum efficiency (Fig. 8) makes it possible to consider the n-Bi$_2$O$_3$/p-CuBi$_2$O$_4$/p-CuO heterostructures as promising photocathodes in photoelectrochemical cells for water splitting.

Acknowledgments This work was supported by project no. AP05130392 “Increasing of energy efficiency of photoelectrochemical solar cells due to application of new semiconductor materials” within the state program no. 217 “Development of Science” (the subgroup 102) of the Republic of Kazakhstan. We are grateful to Dr. Vidas Pakstas from the Center for Physical Sciences and Technology (Vilnius, Lithuania) and Yauhen Anisikevich (Belarusian State University) for their help in taking the SEM images.

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