



# Does the low optical band gap of yellow $\text{Bi}_3\text{YO}_6$ guarantee the photocatalytical activity under visible light illumination?

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Received: 25 September 2017 / Revised: 6 February 2018 / Accepted: 7 February 2018 / Published online: 19 February 2018  
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## Abstract

$\text{Bi}_3\text{YO}_6$ , which is known as an ionic conductor, was tested here as an electrode and photoanode in contact with aqueous electrolytes.  $\text{Bi}_3\text{YO}_6$  was deposited onto the Pt substrate and the such prepared electrode was polarized in various aqueous electrolytes. The optical energy band gap of the material equal to 1.89 eV was determined using the Kubelka-Munk function resulting from the UV-Vis spectrum (allowed indirect transition) and also was calculated using the semi-empirical PM7 method (3.38 eV of HOMO-LUMO energy gap). Despite the yellow color of  $\text{Bi}_3\text{YO}_6$ , the tested material exhibits photoelectroactivity only in the UV range of electromagnetic radiation. The anodic photocurrent characteristic for n-type metal oxide semiconductors was recorded. The electrode exhibits diffusion-controlled cathodic activity while polarized in chloride-free aqueous electrolytes.

**Keywords**  $\text{Bi}_3\text{YO}_6$  · Semiconductor · Aqueous electrolyte · Photoactivity · Photoanode

## Introduction

Metal oxides are known to be used in many electrochemical-based devices such as gas sensor, biosensor, and chemical sensor [1], optical sensors [2], lithium ion batteries [3], photoanodes [4], and environmental remediation photocatalysts [5]. A group of bismuth inorganic compounds such as  $\text{Bi}_2\text{O}_3$ ,  $\text{BiVO}_4$ , BIMEVOX,  $\text{BiMoO}_6$ ,  $\text{BiOCl}$ , and  $\text{Bi}_2\text{WO}_6$  are known to act as electrode materials, exhibiting high electrical capacity, chemical stability under multiple polarization cycles, photoelectroactivity, and photocatalytical properties [6–11].

**Electronic supplementary material** The online version of this article (<https://doi.org/10.1007/s10008-018-3918-y>) contains supplementary material, which is available to authorized users.

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Their potential applications spread from supercapacitors to photoelectrochemical cells for water splitting or water pollutant degradation. Some of these compounds belong to high temperature solid state electrolytes, having a structure allowing oxygen ions mobility to occur.

The  $\delta\text{-Bi}_2\text{O}_3$  is a high temperature polymorph of bismuth oxide [12]. The significant decrease of ionic conductivity at lower temperatures is observed due to the phase transition of cubic  $\delta$ -phase to  $\alpha$ ,  $\beta$ , or  $\gamma$  polymorphs. Great effort has been made to preserve the high-conducting structure at lower temperatures. It can be achieved via partial substitution of Bi atoms in  $\text{Bi}_2\text{O}_3$  by, e.g., rare earth metals [13], which leads to the formation of a series of new compounds with new properties. One of them is  $\text{Bi}_3\text{YO}_6$  that occurs in the  $\delta$ -phase even at room temperature [14]. The defect structure, vacancy ordering, and oxygen ion transport in the  $\text{Bi}_3\text{YO}_6$   $\delta$ -phase were studied using ab initio molecular dynamic, as well as total neutron scattering analysis [15–17]. Ionic transport in a material and its defect structure are commonly tested in  $\text{Bi}_3\text{NbO}_7\text{-Bi}_3\text{YO}_6$  systems [18, 19] and in tungsten-doped  $\text{Bi}_3\text{YO}_6$  [20].

Some of bismuth-containing solid electrolytes which are characterized by high ionic conductivity may exhibit also gas sensing properties [21] or be tested as solid membranes for gas separation [22]. Such materials in contact with aqueous electrolytes may show completely new features. The materials from the  $\text{Bi}_2\text{O}_3\text{-V}_2\text{O}_5\text{-Me}_x\text{O}_y$  system (BIMEVOX) are a good

example. It was reported that BIMEVOX layers deposited onto the conductive substrate exhibit photoelectrochemical activity and may be used as photoanodes [8, 23, 24]. The unique electronic structure of Bi-containing oxides characterized by a well spread valence band consisting of Bi 6s and O 2p orbitals makes them good candidates for being visible-light active photocatalysts [25]. Materials in the form of powder were tested also as catalysts active under visible light illumination, able to photodegrade organic contaminations [26, 27] and photoreduce Cr (VI) [28]. Thus, materials which are known as solid electrolytes and exhibit outstanding ionic conductivity should be tested and exploited as semiconductors at low temperatures in contact with aqueous electrolytes. We focus on these compounds which exhibit optical properties, suggesting their activity under visible light illumination in respect to photoelectroactivity—semiconductors with a narrow energy band gap. Such a material is tested here—the yellow in color Bi<sub>3</sub>YO<sub>6</sub> double oxide known as a high temperature solid state electrolyte [14].

In the present work, Bi<sub>3</sub>YO<sub>6</sub> powder was deposited onto a conductive substrate and tested as an electrode. The influence of electromagnetic radiation on electrochemical performance of prepared electrodes was studied. The films of Bi<sub>3</sub>YO<sub>6</sub> on Pt substrate were used as photoanodes for photoelectrocatalytical oxidation of water. The structure, surface, and optical properties were tested using XRD, FT-IR, XPS, and UV-Vis, respectively.

## Experimental

### Apparatus

Ambient temperature X-ray powder diffraction data were collected on a Philips X'Pert Pro X-ray diffractometer fitted with an X'Celerator detector, using Ni filtered Cu-K $\alpha$  radiation ( $\lambda_1 = 1.54056 \text{ \AA}$  and  $\lambda_2 = 1.54439 \text{ \AA}$ ), in flat plate  $\theta/\theta$  geometry on a spinning sample holder. Data collection was carried out the range  $5\text{--}125^\circ 2\theta$ , in steps of  $0.0167^\circ$ , with an effective scan time of 50 s per step. Calibration was carried out with an external LaB<sub>6</sub> standard.

The UV-Vis spectra of Bi<sub>3</sub>YO<sub>6</sub> were recorded using a dual beam UV-Vis spectrophotometer (Lambda 35, Perkin-Elmer) equipped with a diffuse reflectance accessory. FT-IR analyses were carried out by using a Nicolet 8700 FT-IR spectrometer equipped with an attenuated total reflectance (ATR) accessory. The morphology of the Bi<sub>3</sub>YO<sub>6</sub> layers was investigated by the Schottky field emission scanning electron microscope (FEI Quanta FEG 250) with an ET secondary electron detector. The beam accelerating voltage was kept at 15 kV. Electrochemical and photoelectrochemical experiments (cyclic voltammetry,

electrochemical impedance spectroscopy, chronoamperometry) were performed using the AutoLab PGStat10 potentiostat-galvanostat system under GPES 4.9 software control. Electrochemical impedance spectroscopy (EIS) measurements were recorded in 0.2 M KCl and 0.1 M K<sub>2</sub>SO<sub>4</sub> in the 20 kHz–0.1 Hz frequency range at rest potential. The fitting procedure was performed using EIS spectrum analyzer software. Three types of elements were utilized to prepare the electrical equivalent circuit: *R*—resistor, *CPE*—constant phase element, and *W<sub>o</sub>*—Warburg open element (the impedance of finite-length diffusion with reflective boundary).

Impedance of the constant phase element is defined as:

$$Z(\omega) = P^{-1}(j\omega)^{-n} \quad (1)$$

and impedance of the Warburg open element is given by the formula:

$$Z_{W_o}(\omega) = \frac{W_{or}}{\sqrt{\omega}}(1-j)\coth\left[W_{oc}\sqrt{j\omega}\right] \quad (2)$$

Measurements carried out under illumination were performed in a photoelectrochemical cell equipped with a quartz window. The geometrical surface area of the electrodes was equal to  $\sim 0.5 \text{ cm}^2$ . A high-pressure 150-W xenon lamp (Osram XBO 150) with and without the AM1.5 filter was used as a source of electromagnetic radiation. The light intensity was adjusted to  $100 \text{ mW cm}^{-2}$  (with the AM1.5 filter) and  $160 \text{ mW cm}^{-2}$  (without the AM1.5 filter) and was controlled by an Ophir power meter. All electrochemical measurements were carried out at room temperature  $21^\circ \text{C}$ . XPS analysis was performed for three Pt/Bi<sub>3</sub>YO<sub>6</sub> samples before and after polarization in K<sub>2</sub>SO<sub>4</sub> electrolyte using Escalab 250Xi from Thermo Fisher Scientific. In order to normalize spectroscopic measurements, the *x* axis (binding energy) from the XPS spectrum was calibrated for peak characteristics for carbon 1s (284.6 eV). Data analysis was performed using Avantage software provided by the manufacturer. One sample was electrooxidized (60 min at  $E = 0.9 \text{ V}$ ), the second one was electroreduced (60 min at  $E = -0.85 \text{ V}$ ), and the last one was not polarized.

### Chemicals

Li<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, Cs<sub>2</sub>SO<sub>4</sub>, KCl, and KNO<sub>3</sub> used as electrolytes were of analytical grade and were supplied by POCH. Bi<sub>2</sub>O<sub>3</sub> (99.9%) and Y<sub>2</sub>O<sub>3</sub> (99.99%) used for material synthesis were supplied by Sigma Aldrich.

### Synthesis

Bi<sub>3</sub>YO<sub>6</sub> was synthesized by conventional solid state reaction technique. Sample of Bi<sub>3</sub>YO<sub>6</sub> was prepared using

stoichiometric amounts of  $\text{Bi}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ . The starting mixtures were ground in ethanol using a planetary ball mill. The dried mixtures were heated at  $740^\circ\text{C}$  for 24 h, then slowly cooled and reground. The sample was then reheated at  $800^\circ\text{C}$  for further 24 h before slow cooling in air to room temperature, over a period of approximately 5 h.

## Electrode preparation

$\text{Bi}_3\text{YO}_6$  powder was deposited onto the platinum foil using the dip-coating method. First, 0.2 g of material and about 0.1 g of poly(ethylene oxide—PEO) ( $M = 300,000$ , Aldrich) were mixed with 1 ml of water. The platinum foil was immersed in the resulting suspension, pulled out, dried, and heated for 5 h at  $400^\circ\text{C}$  in an air atmosphere (with a heating rate of  $1^\circ\text{C min}^{-1}$ ). The annealing procedure was performed in a quartz tube using a Czylok PRC 55 L/1300 M furnace.

To avoid contact of the studied material with PEO, some of the electrodes were prepared using a glass capillary filled with  $\text{Bi}_3\text{YO}_6$ , where the Pt wire was used as an electrical contact. To test the influence of binder on the photoelectrochemical properties, some of the electrodes were prepared by drop-casting of the  $\text{Bi}_3\text{YO}_6$  water suspension on the platinum foil and then dried at  $100^\circ\text{C}$ .

## Results

### Powder and electrode characterization

#### SEM

The morphology of the layer, deposited using the proposed method, is dependent on the morphology of the starting powder. Scanning electron micrographs of the  $\text{Bi}_3\text{YO}_6$  layer are presented in Fig. 1a, b. The method of deposition allows a compact film build by  $\text{Bi}_3\text{YO}_6$  coarse grains to be obtained. Clearly visible pores between the grains were formed during

$\text{CO}_2$  evolution during thermal degradation of the binder (PEO). The grain size determined using the SEM technique is in the range between about 500 and 2500 nm.

#### XRD

The XRD patterns of  $\text{Bi}_3\text{YO}_6$  for the powder sample and the deposited layer are presented in Fig. 2. Both patterns were collected at room temperature and consist of a set of peaks at the same positions. All peaks in the diffraction patterns can be indexed on a cubic  $Fm\bar{3}m$  cell, with no evidence for phase separation. The preservation of the cubic form after the deposition procedure can be concluded. Structure refinement was carried out by Rietveld fitting of X-ray data set using the program GSAS [29]. For the cubic phase, a fluorite model in space group  $Fm\bar{3}m$  was used: Bi and Y were located on the ideal  $4a$  site (0,0,0), with oxide ions initially distributed over three sites:  $8c$  at (0.25, 0.25, 0.25);  $32f$  at approximately (0.3, 0.3, 0.3), and  $48i$  at around (0.5, 0.2, 0.2). A total oxide ion occupancy constraint was applied. Calculated unit cell dimension is  $5.49458(9) \text{ \AA}$ .

#### ATR FT-IR

Samples of the material in the form of a layer and powder were compared using ATR FT-IR spectroscopy. Spectra of  $\text{Bi}_3\text{YO}_6$  are characterized by a very intensive peak below  $750 \text{ cm}^{-1}$  wavenumbers (see Fig. 3), which is characteristic for metal-oxygen vibrations [30]. In the case of the  $\text{Bi}_3\text{YO}_6$  layer, additional low intensity peaks at 832 and 857, 1112, 1399, and  $1497 \text{ cm}^{-1}$  were recorded. Two peaks in the  $830\text{--}860 \text{ cm}^{-1}$  range are probably related to O–H deformation vibrations of different bonded OH groups. The peak near  $860 \text{ cm}^{-1}$  was previously described in the  $\text{Y}_2\text{O}_3\text{--B}_2\text{O}_3\text{--Bi}_2\text{O}_3$  system as  $[\text{BiO}_3]$  unit vibrations [31] and the Bi–O vibration in distorted  $\text{BiO}_6$  units [32]; however, such peak was not recorded for the material in the form of powder. The peak at  $1112 \text{ cm}^{-1}$  may originate from C–O–C stretching vibrations as the residue of

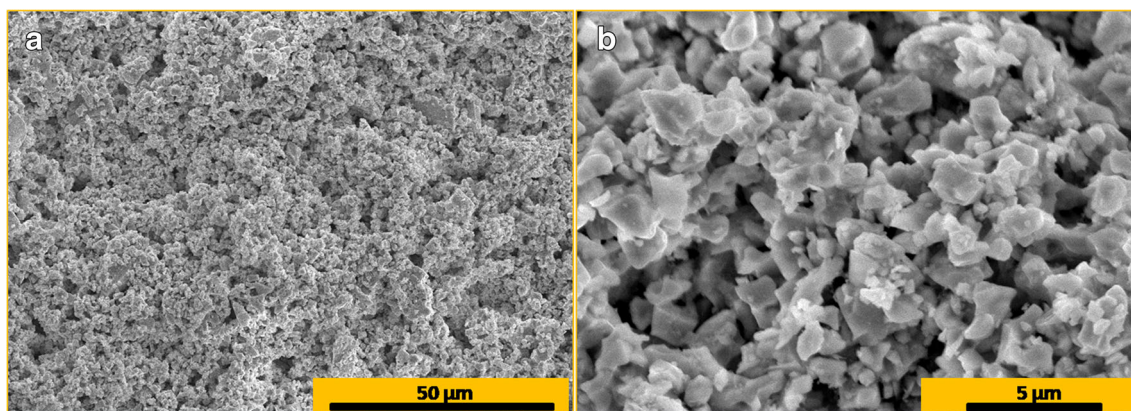
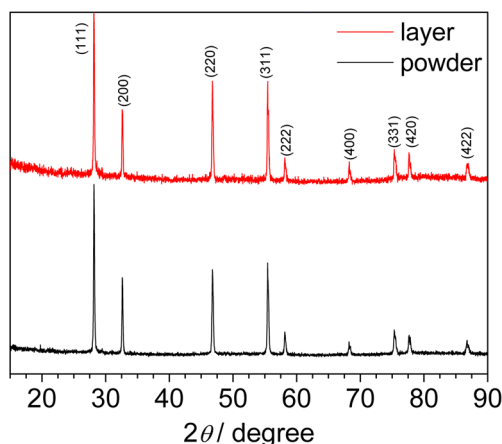


Fig. 1 Scanning electron micrographs of  $\text{Bi}_3\text{YO}_6$  layers deposited onto the Pt substrate using the dip-coating method

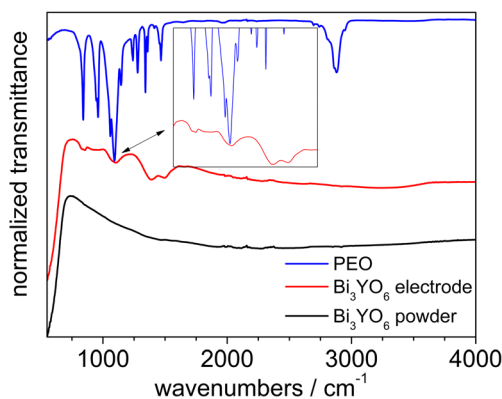


**Fig. 2** XRD patterns of  $\text{Bi}_3\text{YO}_6$  for the powder sample and deposited layer

the binder, and peaks in the range between  $1400$  and  $1500\text{ cm}^{-1}$  could be described as C–H deformation vibrations, but no C–H stretching vibrations near  $3000\text{ cm}^{-1}$  were recorded. Additionally, a broad, low intensity band at  $3000\text{--}3500\text{ cm}^{-1}$  from O–H stretching vibrations was found. The IR spectrum of PEO is presented for comparison. As it may be concluded, all peaks recorded for the  $\text{Bi}_3\text{YO}_6$  layer in the range between  $750$  and  $1650\text{ cm}^{-1}$  originate from the binder used. Even after prolonged annealing, residues of organic polymer remain on the surface of the deposited material. To sum up, the crystal structure of the material remains unchanged, but the surface of  $\text{Bi}_3\text{YO}_6$  is slightly modified due to contact with PEO during layer annealing.

### UV-Vis spectroscopy

Optical properties of  $\text{Bi}_3\text{YO}_6$  were examined using UV-Vis spectroscopy in the reflectance mode. Spectra of both samples (powder and layer) are presented in Fig. 4a. Absorption starts at about  $\sim 650\text{ nm}$  and has a maximum at  $\sim 405\text{ nm}$ . The material absorbs a significant part of visible light, which is a good characteristic of materials that may be used in

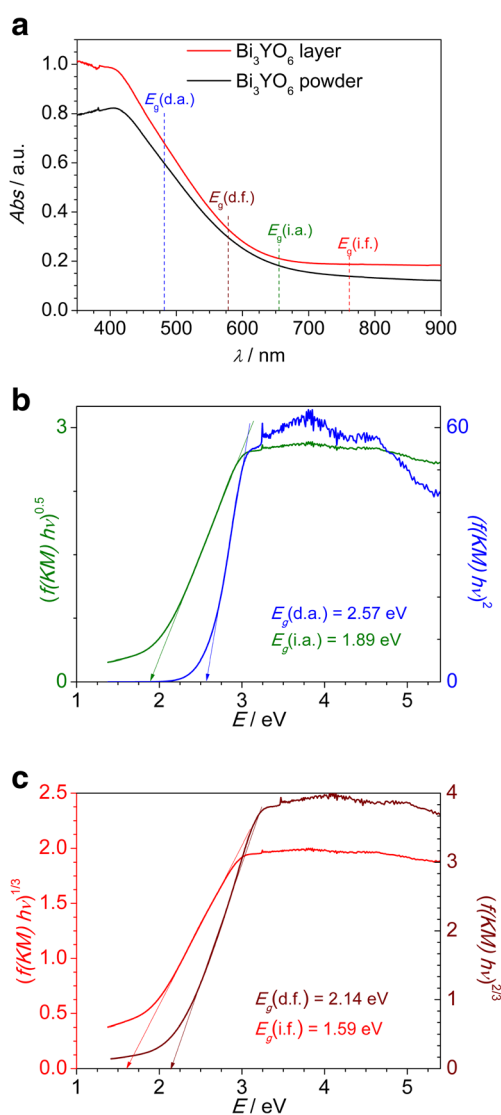


**Fig. 3** The comparison of ATR FT-IR spectra of PEO,  $\text{Bi}_3\text{YO}_6$  powder, and  $\text{Bi}_3\text{YO}_6$  layer

photocatalysis. The Kubelka-Munk function (Eq. 3) [33] was applied to determine the energy band gap of the tested material.

$$f(KM) = \frac{(1-R)^2}{2R} \quad (3)$$

The energy band gap was determined by extrapolation of the linear region of  $(f(KM) h\nu)^n$  vs.  $h\nu$  and taking an intercept on the  $x$  axis. The power “ $n$ ” is dependent on the type of electron transition ( $n=2$ —direct allowed (d.a.),  $n=0.5$ —indirect allowed (i.a.),  $n=2/3$ —direct forbidden (d.f.),  $n=1/3$ —indirect forbidden (i.f.)) [34]. All possibilities (direct and indirect, allowed and forbidden) for the material in the form of powder and layers were negligible as presented in Fig. S1 in



**Fig. 4** **a** UV-Vis spectra of  $\text{Bi}_3\text{YO}_6$  layer and powder. Inset: The photograph of  $\text{Bi}_3\text{YO}_6$  powder. **b**  $(f(KM) h\nu)^2$  and  $(f(KM) h\nu)^{0.5}$  vs.  $h\nu$  plots and **c**  $(f(KM) h\nu)^{1/3}$  and  $(f(KM) h\nu)^{2/3}$  vs.  $h\nu$  plots resulting from the UV-Vis spectrum of  $\text{Bi}_3\text{YO}_6$  powder

supporting information). The linear region of  $(f(KM) \cdot h\nu)^n$  vs.  $h\nu$  function can be found in all cases. The estimated values of energy band gaps for each case are marked with an appropriate color on the UV-Vis spectrum in Fig. 4a. There are materials which exhibit two types of transitions [35, 36]. However, taking into account the UV-Vis spectrum in Fig. 4a, absorption starts to rise near 656 nm, which is the value that corresponds to 1.89 eV. Thus, it is very likely that the optical band gap of tested material is related to the allowed indirect transition. The determined value of an energy band gap allowing visible light absorption makes  $\text{Bi}_3\text{YO}_6$  interesting from the photocatalytical point of view. Nevertheless, optical properties of the studied material should be further examined to describe them in more detail.

The energy band gap of tested material has been also determined using semi-empirical PM7 calculations under LS (Singlet) Born–von Kärman periodic boundary conditions [37] implemented in MOPAC2016, Version: 17.119W package by James J. P. Stewart [38] at experimental geometry of cubic  $\delta$ -type phase of  $a = 5.496 \text{ \AA}$ . Surprisingly, the calculated value of  $E_g$  of  $\text{Bi}_3\text{YO}_6$  is equal to 3.38 eV. This value is 1.49 eV higher than the value of the indirect gap determined from the UV-Vis spectrum. The average unsigned error of PM7 calculated ionization energy in sets of reference compounds ([http://openmopac.net/PM7\\_accuracy/molecules.html](http://openmopac.net/PM7_accuracy/molecules.html)) is 0.55 eV. Such a big difference between determined values may then result from the surface properties of  $\text{Bi}_3\text{YO}_6$ . Exclusion of the influence of absorption by impurities or surface electronic states cannot be unambiguously done [39]. For example, as it was previously shown for yttrium-doped  $\text{BiVO}_4$  ( $\text{Bi}_x\text{Y}_{1-x}\text{VO}_4$ ), a surface of bismuth-containing metal oxide is mainly built by  $\text{BiO}_y$  units [40]. Their presence allows the part of visible light to be absorbed; however, the bulk material is characterized by a different electronic structure and absorbs only UV light.

## Electrode characterization

### Electrochemical properties

Cyclic voltammetry curves of  $\text{Pt}/\text{Bi}_3\text{YO}_6$  polarization in contact with aqueous electrolytes are presented in Fig. 5. Figure 5a consists of CV curves recorded in 0.1 M  $\text{K}_2\text{SO}_4$  using different scan rates ( $10\text{--}100 \text{ mV s}^{-1}$ ). The peak “A” is characteristic for metal oxides electrodes and is associated with the anodic plateau “B.” The mentioned electroactivity is related to the surface species present on the hydrated surface of the material, which is in contact with water [41]. Similar processes were observed for titanium dioxide electrodes in previous reports [42, 43]. Anodic peaks marked as “C” and the cathodic peak “D” are characteristic for  $\text{Bi}_3\text{YO}_6$ . The anodic current density maximum shows a linear relation with the scan rate (see Fig. 5b). Interestingly, the current density of the

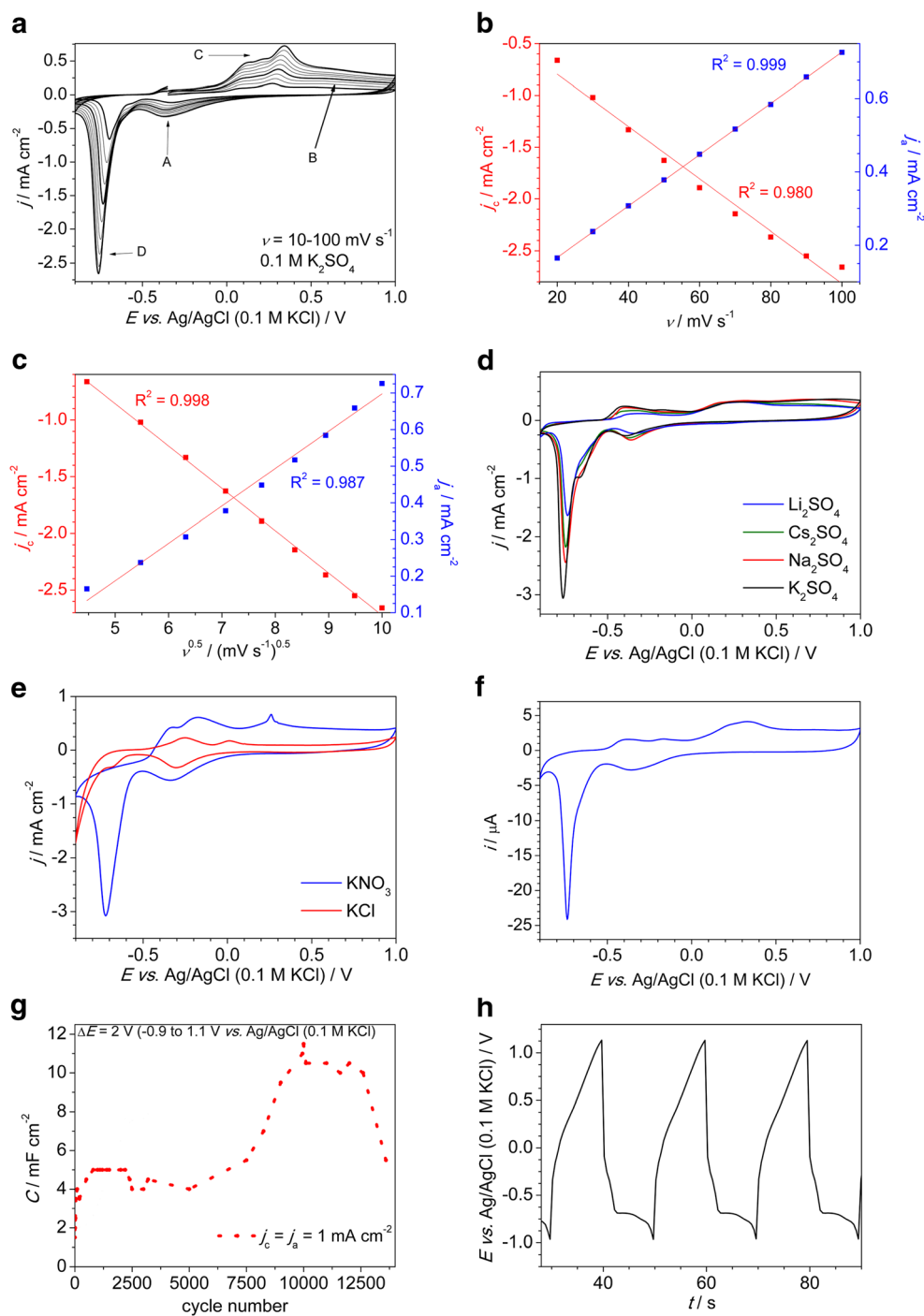
cathodic peak shows a linear relation with the square root of the scan rate, suggesting process control by diffusion (Fig. 5c). Some of metal oxides exhibit cathodic electroactivity (diffusion controlled) in aqueous electrolytes related to the cation insertion to the oxide structure, e.g.,  $\text{MnO}_2$  [44]. Additional tests were performed in electrolytes containing various cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ). CV curves are presented in Fig. 5d. As it can be seen, the size of the cation does not affect the cathodic current density; thus, the observed process is not related to the ion insertion into  $\text{Bi}_3\text{YO}_6$ . The ex-situ measured XRD pattern (see Fig. S2 in supporting information) of the cathodically polarized electrode is the same as for the electrode before electrochemical tests, so electrochemical polarization does not affect the crystal structure of the studied material. Peaks observed on the CV curve are probably related to the surface group activity. Noteworthy, similar peaks were recorded in 0.2 M  $\text{KNO}_3$  but were not recorded during electrode polarization, which was immersed in a chloride-containing electrolyte (0.2 M  $\text{KCl}$ ) as it is shown in Fig. 5e. The presence of  $\text{Cl}^-$  anions in the electrolyte which adsorb on the electrode surface deactivates electroactive groups on the surface of  $\text{Bi}_3\text{YO}_6$ . The cathodic current recorded at  $\sim -0.8 \text{ V}$  is related to the irreversible reduction of the material in  $\text{KCl}$  aqueous electrolyte. Long-term cathodic polarization of  $\text{Bi}_3\text{YO}_6$  in  $\text{KCl}$  aqueous electrolyte leads to layer darkening. Two small peaks recorded when the electrode was polarized in the anodic direction may be related to partial two-step oxidation of metallic bismuth [45].

The electroactivity recorded in sulfate- and nitrate-containing electrolytes is not related to the surface groups observed on the FT-IR spectrum and formed during layer preparation. An additional cyclic voltammetry curve was recorded for the electrode prepared without PEO (using a glass capillary filled with  $\text{Bi}_3\text{YO}_6$  and a platinum wire as the electrical contact). CV is presented in Fig. 5f. As it can be seen, the shape of the curve is the same as in the case of the electrodes prepared by the dip-coating method; thus, the used method of film deposition does not affect  $\text{Bi}_3\text{YO}_6$  electroactivity.

The  $\text{Pt}/\text{Bi}_3\text{YO}_6$  was tested as a potential electrode for energy storage devices. The capacitance was calculated from multiple galvanostatic ( $1 \text{ mA cm}^{-2}$ ) charge/discharge cycles recorded in 0.1 M  $\text{K}_2\text{SO}_4$  presented in Fig. 5g. Multiple chronopotentiometry curves allow the electrochemical stability to be tested. The capacitance is relatively stable during the first 6000 cycles and then surprisingly increases reaching the value of  $10.5 \text{ mF cm}^{-2}$  ( $\sim 500 \text{ mF g}^{-1}$ ,  $\sim 2100 \text{ mF cm}^{-3}$ ) as it is shown in Fig. 5h. It may be related to the penetration of the layer pores with electrolyte. Material started to lose its capacitance after 12,500 cycles which indicates high electrostability of the tested  $\text{Bi}_3\text{YO}_6$  electrode.

The influences of electrolytes used ( $\text{K}_2\text{SO}_4$  and  $\text{KCl}$ ) on the electrical properties of the  $\text{Pt}/\text{Bi}_3\text{YO}_6$  electrode and electrode/

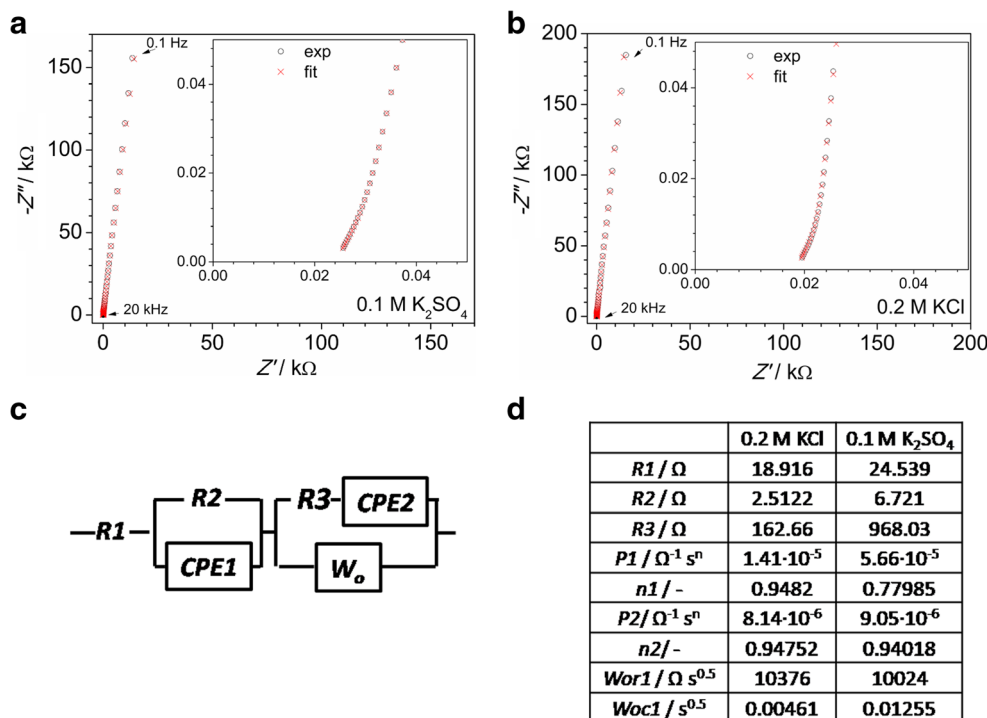
**Fig. 5** **a** CV curves of Pt/Bi<sub>3</sub>YO<sub>6</sub> electrode in 0.1 M K<sub>2</sub>SO<sub>4</sub>. Scan rates 10–100 mV s<sup>-1</sup>. Dependence of current density of anodic and cathodic maxima **b** vs. scan rate and **c** vs. square root of the scan rate. **d** CV curves of Pt/Bi<sub>3</sub>YO<sub>6</sub> electrodes registered in different electrolytes (Li<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, and Cs<sub>2</sub>SO<sub>4</sub> (scan rate—100 mV s<sup>-1</sup>). **e** The comparison of CV curves of Pt/Bi<sub>3</sub>YO<sub>6</sub> recorded in KNO<sub>3</sub> and KCl (scan rate—100 mV s<sup>-1</sup>). **f** CV curve of Bi<sub>3</sub>YO<sub>6</sub> electrode prepared without polyethylene oxide (scan rate—100 mV s<sup>-1</sup>). **g** The chronopotentiometry curves ( $j_c = j_a = 1 \text{ mA cm}^{-2}$ ). **h** Resulting capacitance vs. number of cycle plot



electrolyte interface were investigated using electrochemical impedance spectroscopy. The impedance spectra recorded in both electrolytes were recorded at rest potential and are shown in Fig. 6a, b. As it is presented, the spectra are very similar. A fitting procedure using the equivalent circuit (EQC) presented in Fig. 6c was performed. The EQC consists of six elements as it is shown in Fig. 6c. The  $R1$  resistor represents the electrolyte and external contact resistance. The constant phase element ( $CPE1$ ) and resistor  $R2$  are probably related with charge

transfer at the electrolyte/electrode interface. The second constant phase element ( $CPE2$ ) connected in parallel with resistor  $R3$  and Warburg element ( $W_o$ ) can be interpreted as related to the grain boundary resistance and diffusion in pores. It is consistent with the morphology of the film as it is presented on the SEM micrographs (see Fig. 1). The results of the fitting procedure in the form of table are presented in Fig. 6. As it may be concluded, the “bulk” properties of the electrode (elements  $R3$  and  $CPE2$ ) do not change significantly with the electrolyte

**Fig. 6** The registered “o” and fitted “x” impedance spectra of Pt/Bi<sub>3</sub>YO<sub>6</sub> electrode recorded in **a** 0.1 M K<sub>2</sub>SO<sub>4</sub> and **b** 0.2 M KCl at rest potential. **c** The electrical equivalent circuit used in EIS analysis and the table with the obtained results and d values of parameters of equivalent circuit



used. However, the change of the *R2* and *CPE2* elements is clear. The resistance on the electrolyte/electrode interface is almost six times higher in the case of K<sub>2</sub>SO<sub>4</sub> electrolyte. It can be related to the hydroxylation of the surface of the electrode and formation of surface groups, which is consistent with CV curves recorded in chloride- and sulfate-containing electrolytes. Moreover, the differences of the value of “*P*” parameter in the *CPE2* element indicate changes in the electrical double layer capacitance. Thus, the presence of chlorides affects the electrode/electrolyte interface and affects the electrochemical properties of Pt/Bi<sub>3</sub>YO<sub>6</sub>.

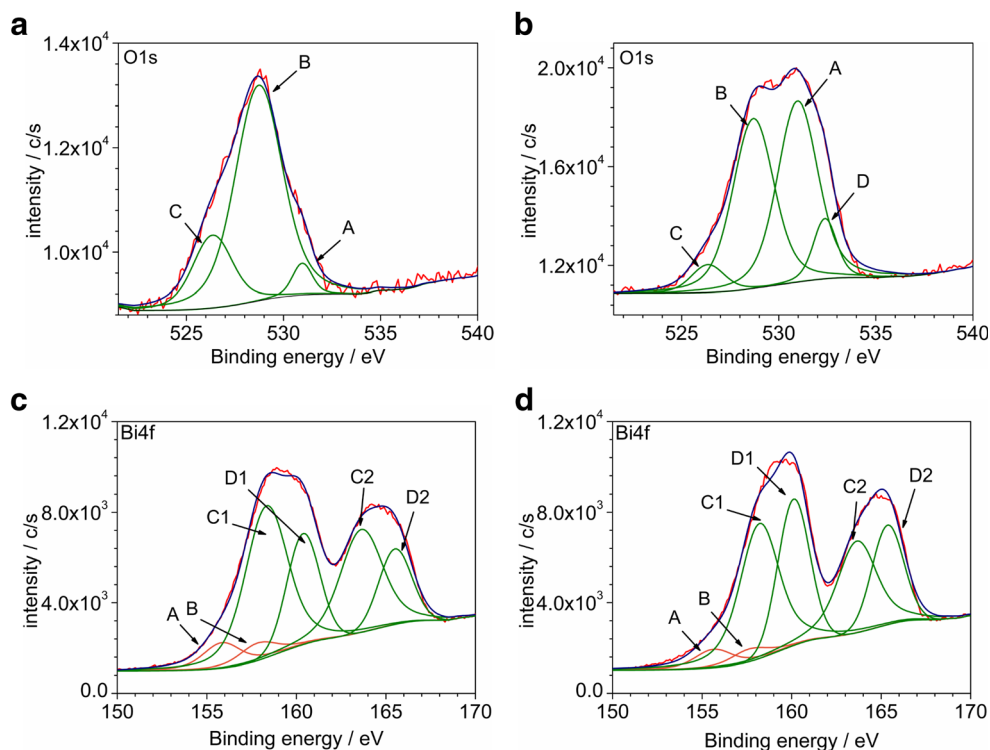
**XPS analysis**

XPS analysis was performed to find changes in chemical surface stages of Bi, Y, and O induced by polarization of the Pt/Bi<sub>3</sub>YO<sub>6</sub> electrodes. In all cases, except the sample after anodic polarization in K<sub>2</sub>SO<sub>4</sub> electrolyte, the energy range characteristic for the O1s orbital was fitted using three oscillators. An exemplary spectrum of a layer is presented in Fig. 7a. The peak at the highest binding energy (530.9 eV) marked as A can be assigned to OH groups as it was shown in the case of other metal oxides [46, 47]. The second one (B) at 528.7 eV is probably observed due to the presence of lattice metal-oxygen bonds [48–50]. The third peak (C) at 526.3 eV may be related to carbon-containing contaminations. Unfortunately, cleaning of the surface using the argon-ion sputtering procedure cannot be applied for these types of samples. The Ar<sup>+</sup> beam significantly affects the XPS spectrum in an energy range characteristic for

bismuth. The phenomenon of metal reduction due to Ar<sup>+</sup> treatment was already observed for other metal oxides, e.g., CuO [51], TiO<sub>2</sub> [52, 53], and MoO<sub>3</sub> [54]. In the case of electrooxidized samples, an additional peak marked as D at 532.4 eV has been found (see Fig. 7b). It indicates that anodic polarization (0.9 V, 60 min) leads to the formation of oxygen-rich surface groups which are the precursors of oxygen evolution, as it was previously reported for a preilluminated TiO<sub>2</sub> photoanode [41]. In the case of the electrooxidized sample, also the relative intensity of the peak A increased significantly suggesting formation of new OH groups on the surface of the electrode.

The doublet characteristic for yttrium 3d orbital overlaps with the signal from Bi 4f, as it is shown in Fig. 7c. After deconvolution of all samples’ spectra, positions of peaks at 155.7 eV (A) and 158.1 eV (B) were shifted slightly (± 0.4 eV) between the samples and no new peak characteristic for yttrium appeared after electrochemical treatment. More detailed analysis of the Y 3d orbital is very difficult due to the low intensity of peaks in comparison with overlapping Bi 4f peaks. Polarization of Pt/Bi<sub>3</sub>YO<sub>6</sub> does not clearly affect Y atoms in the samples. However, changes of the peaks coming from the Bi 4f orbital can be found. The intensity and area ratios of the peaks marked as C1 (158.3 ± 0.2 eV), C2 (163.6 ± 0.1 eV), D1 (160.3 ± 0.1 eV), and D2 (165.5 eV) change as it is shown for the samples electrooxidized and electroreduced in K<sub>2</sub>SO<sub>4</sub> electrolyte (see. Fig. 7c, d). Two doublets of the Bi 4f orbital were already reported, e.g., for Bi<sub>2</sub>O<sub>2.33</sub> [55] and Bi<sub>2</sub>WO<sub>6</sub> [56], and were interpreted as coexistence of Bi<sup>3+</sup> and Bi in the lower oxidation states. It may be

**Fig. 7** The XPS spectra of the **a** as prepared and **b** anodically polarized Pt/Bi<sub>3</sub>YO<sub>6</sub> in the O1s region. The XPS spectra of the **c** reduced and **d** oxidized Pt/Bi<sub>3</sub>YO<sub>6</sub> electrode in the Bi 4f region



concluded that electroactivity recorded on the cyclic voltammetry curves is related to the changes of Bi species on the surface of the electrode. Thus, cathodic polarization of the electrode leads to the formation of the “Bi suboxides” [57, 58] as the increase of the intensity of the peak related to the reduced form of Bi is observed.

### Photoelectrochemical performance

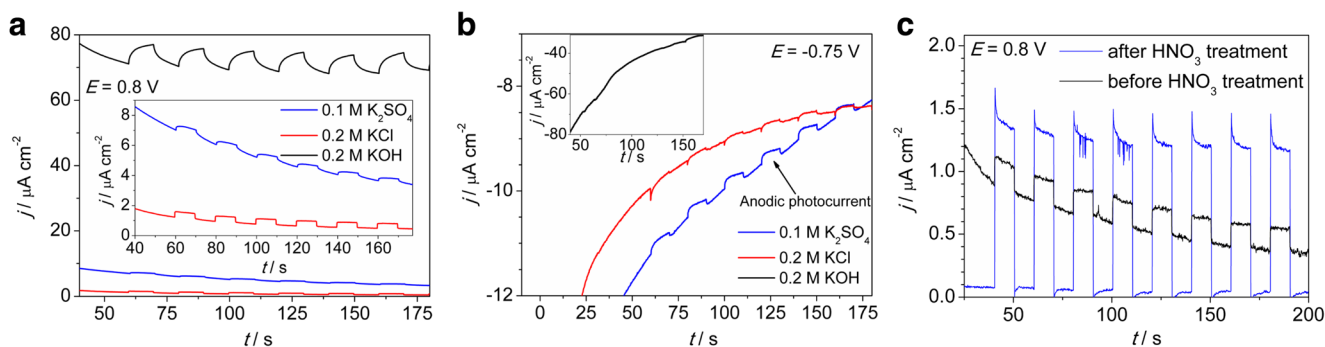
Photoelectrochemical properties of prepared electrodes were examined using the chronoamperometry technique recorded under intermittent illumination. First, the electrode was polarized ( $E = \text{const}$ ) in dark conditions to achieve a steady state current. Then, the electrode was illuminated and the current was measured. In the case of simulated solar light (AM 1.5 filter), the photocurrent was not generated. Despite the material is yellow and exhibits absorption in the visible range of electromagnetic radiation, absorbed photons were not converted to electrical energy. Thus, it is very likely that UV-Vis spectroscopy shows the surface electronic states, but the real, “bulk” energy band gap is higher as it follows from the calculations.

Bi<sub>3</sub>YO<sub>6</sub> exhibited photoactivity, when the electrode was illuminated with whole UV-Vis radiation emitted by the lamp (without AM 1.5 filter). It is in agreement with energy band gap estimated using semi-empirical calculations. The chronoamperometry curves ( $E = 0.8$  V vs. Ag/AgCl (0.1 M KCl)) are shown in Fig. 8a. As it can be seen, the Bi<sub>3</sub>YO<sub>6</sub> film generated anodic photocurrent. It is characteristic for n-type

semiconductors that can act as photoanodes [59]. The same experimental setup was used for testing other photoanodic materials like, e.g., bismuth vanadate and titania nanotubes [60], and recorded photocurrent was even several hundred times higher. The Pt/Bi<sub>3</sub>YO<sub>6</sub> electrodes were also prepared without binder to exclude the influence of pyrolyzed PEO residues on the obtained results. The chronoamperometric curve is presented in supplementary information (see Fig. S3). In both cases, namely for electrode prepared with PEO binder and electrode Bi<sub>3</sub>YO<sub>6</sub> without binder, the recorded photocurrent is in the same range. Thus, the usage of binder does not affect the photoelectrochemical performance of Bi<sub>3</sub>YO<sub>6</sub> films.

The photocurrent recorded when the electrode was immersed in KCl and K<sub>2</sub>SO<sub>4</sub> is comparable and is related to water and/or chloride oxidation. Illumination of the electrode which is in contact with KOH leads to an over 20 times higher photocurrent. OH<sup>−</sup> anions may act as “hole scavengers” because of a lower potential of O<sub>2</sub> evolution in comparison with the water oxidation reaction ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ,  $E = 1.23$  V and  $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ ,  $E = 0.4$  V). The chronoamperometry curves of the Pt/Bi<sub>3</sub>YO<sub>6</sub> electrode at  $E = -0.75$  V vs. Ag/AgCl (0.1 M KCl) are presented in Fig. 8b. In the case of the KOH and KCl electrolyte, the effect of photocurrent generation is not clearly observed. However, the electrode immersed in K<sub>2</sub>SO<sub>4</sub> electrolyte generates an anodic photocurrent even at cathodic potential. The n-type semiconductor can act as a photoanode only when the applied potential is higher (more anodic) than the flat band potential ( $E_{fb}$ ). It





**Fig. 8** Chronoamperometry curves of Pt/Bi<sub>3</sub>YO<sub>6</sub> electrode immersed in K<sub>2</sub>SO<sub>4</sub>, KCl, and KOH recorded under intermittent UV-Vis illumination at **a**  $E = 0.8$  V vs. Ag/AgCl (0.1 M KCl) and **b**  $E = -0.75$  V vs. Ag/AgCl

(0.1 M KCl). **c** The comparison of CA curves recorded at 0.8 V vs. Ag/AgCl (0.1 M KCl)

means that the  $E_{fb}$  is more cathodic than  $-0.75$  V vs. Ag/AgCl (0.1 M KCl); however, the precise value was not evaluated. A routine procedure for  $E_{fb}$  evaluation using Mott-Schottky plot is found in the studied case to be ambiguous due to complexity of the electrode/electrolyte interface in a broad potential range. Surface active species give rise to electrochemical capacitance of Pt/Bi<sub>3</sub>YO<sub>6</sub> electrodes as one may see on CV curves (see Fig. 5).

It was reported that photoactivity of bismuth-containing catalysts may be inhibited due to the BiO<sub>y</sub> clusters on the surface of the oxide. Differences in the electronic structure of the bulk material and the BiO<sub>y</sub>-rich surface lead to the adverse “self-heterojunction” formation [40]. The authors proposed a method of BiO<sub>y</sub> removing from the surface using diluted HNO<sub>3</sub>. Almost four times enhancement of photocatalytic water splitting efficiency was observed after HNO<sub>3</sub> treatment [40]. In the present work, the same method has been utilized to improve photoelectrocatalytic performance of Bi<sub>3</sub>YO<sub>6</sub>. The comparison of chronoamperometry curves recorded during illumination of the Pt/Bi<sub>3</sub>YO<sub>6</sub> photoanode before and after acid treatment is presented in Fig. 8c ( $E = 0.8$  V, 0.1 M K<sub>2</sub>SO<sub>4</sub>). It is clearly seen that HNO<sub>3</sub> treatment leads to photocurrent increase from 0.19 to 1.14  $\mu\text{A cm}^{-2}$ . Thus, acid treatment enhanced not only photocatalytic, but also photoelectrocatalytic properties of Bi-containing metal oxide semiconductors.

## Conclusions

The influence of the deposition procedure on the Bi<sub>3</sub>YO<sub>6</sub> structure and optical properties was presented. The surface of the deposited layer was slightly changed in comparison with the bulk material, as it was presented in IR spectra. The indirect energy band gap of the tested material was estimated to be 1.89 eV using the Kubelka-Munk function, which is a 1.49 eV lower value than that calculated using semi-empirical PM7 calculations. Photoelectrochemical tests under UV-Vis illumination show that the Bi<sub>3</sub>YO<sub>6</sub> film deposited onto Pt foil

may act as a photoanode. An anodic photocurrent was generated in a wide range of applied potentials, proving that the tested material is an n-type semiconductor. It was shown that despite optical energy band gap equals to 1.89 eV, tested material does not generate photocurrent when illuminated with visible light. The electron transition observed on the reflectance spectrum cannot be converted to the photoelectrochemical water oxidation.

The electrode Pt/Bi<sub>3</sub>YO<sub>6</sub> exhibited electrochemical activity related to the changes of the Bi oxidation state when polarized in aqueous electrolytes. However, the reversible cathodic process at  $E = -0.75$  V vs. Ag/AgCl (0.1 M KCl), which is controlled by diffusion, was registered only in Cl<sup>-</sup>-free electrolytes. The influence of electrolyte (KCl and K<sub>2</sub>SO<sub>4</sub>) on electrical properties of the electrode/electrolyte interface was investigated using electrochemical impedance spectroscopy. The lower electrical capacitance was observed in the KCl electrolyte.

**Funding** The financial support provided by the Gdańsk University of Technology DS 032406 is gratefully acknowledged.

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