The influence of the Cu$_2$O deposition method on the structure, morphology and photoresponse of the ordered TiO$_2$NTs/Cu$_2$O heterojunction

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Abstract
The increased interest in highly ordered titania structures exhibiting tubular shape that could be directly formed onto the stable substrate is related with the intensive research on their modification enabling absorption of light within the wide solar spectrum and its further conversion into electric or chemical energy. Among others, formation of uniform 3D heterojunctions based on the TiO$_2$ nanotubes attracts attention since porous structure provides highly developed surface area whereas tubular shape ensures facilitated charge transport. Following that, we focus on the comparison of different electrochemical routes leading to the formation of Cu$_2$O onto the titania nanotubes platform to improve energy harvesting. Proposed approach includes optimized potentiostatic and pulsed polarization of titania immersed in the basic electrolyte composed of Cu$^{2+}$ ions stabilized by lactic acid. In this work, we demonstrate that at strictly selected deposition parameters, namely time, pulse width and cycle number, one can obtain titania nanotubes overgrown by Cu$_2$O species uniformly distributed across the whole TiO$_2$ layer as proved by secondary ion mass-spectrometry. X-ray photoelectron spectroscopy studies indicated purely Cu(I) oxide formation for pulsed deposition route. The photoactivity of obtained materials was verified both under vis and UV–vis irradiation. Depending on the incident light spectrum, variation in photoactivity was observed that is directly related with the charges generation and their transport within the junction. The transient photocurrent measurements show strong photocurrent enhancement for Cu$_2$O modified titania comparing to pristine support and satisfactory photostability under visible light without any protective coating.

1. Introduction
Facing enormous greenhouse-gases emittance and associated global warming problem, nowadays world is in sore need of new, environmentally harmless methods of energy production. Sun radiation is one of the most promising renewable energy sources. Taking into account that the energy of the solar radiation that reaches Earth surface is over 3 orders of magnitude higher than global annual use of energy [1], a great potential in solar-to-electrical conversion technology becomes clear. Therefore, finding new photoactive materials or the modification of those active in the narrow wave spectrum is a challenge for scientists all over the world.

Titanium dioxide nanotubes (TiO$_2$NTs) arrays in the anatase form have been proved to possess excellent photoelectrochemical properties, finding application not only in photovoltaics [2], but also in photocatalysis [3], photoelectrocatalysis [4], supercapacitors [5] or water splitting [6]. Their exceptionally high performance in energy conversion is attributed to the specific architecture of nanotubes’ array and the elongated shape of a single
nanotube, which increases the diffusion length by impeding the recombination of excited electrons [7]. Nevertheless, irrespective of the morphology, band gap of crystalline titania corresponds to its activity in the UV light. Thus, in order to widen the absorption range, one of the strategy is to modify TiO$_2$ by transition metals, such as platinum [8], gold and silver [9], nickel [10] and copper [11] in the form of dopant ions, single nanoparticles and if possible oxide species. Among these metals, the prize of copper is the lowest, while its electrical conductivity is circa 18.5% higher than the one of platinum and only 3% lower than silver [12]. Following that, many works were carried out towards integration of copper species with TiO$_2$ nanotubes and formation of the material exhibiting enhanced response under visible light [13–15], ability to efficient photocatalytic removal of nitrate [16] or CO$_2$ reduction via Z–scheme mechanism [17].

However, considering Cu modification, it should be reminds that copper is likely to oxidize in ambient atmosphere conditions. Those copper oxides are generally characterized by lower electrical conductivity comparing to metal [18]. Depending on the fabrication conditions Cu, CuO or Cu$_2$O could be obtained, but the most stable is copper (II) oxide [19]. However, only pure Cu$_2$O is required to ensure enhanced photoactivity while inclusions of Cu and CuO may even impede the performance of the material [20]. Deposition of Cu$_2$O because of its narrow direct band gap of 1.9–2.2 eV [19] that covers visible wave spectrum may enhance composite photosresponse upon solar irradiation. Furthermore, its p-type character is beneficial for obtaining p–n heterojunction with n-type substrate that affects efficient charge separation. Copper oxide can be obtained by various methods such as dip–coating [21], electrodeposition [22, 23], precipitation [24] and floating zone technique [25]. Among those approaches, electrodeposition is regarded as a most controllable procedure since via changes of electrolyte composition or deposition parameters the amount of material or its morphology could be easily tuned. The main component of the electrolyte is a copper precursor obtained by dissolving the inorganic salts: copper sulphate, nitrate or acetate. Moreover, according to Liu et al. [26] accompanying anions enable design of metal/ metal oxide microcrystals with various shapes and facets. Additionally, stabilizing agents like lactic acid [27] or sodium dodecyl sulphate acting as surfactants [28] are present to block some active sites and introduce heterogeneous impurities. It is also of key importance that this method allows to deposit Cu$_2$O not only onto the flat substrates (glass plate coated by conducting fluorine doped tin oxide, glassy carbon) but also on the semiconducting porous platforms like nanorods, walls and tubular structures [29]. Among others, highly ordered titanium dioxide nanotubes were successfully modified by Cu$_2$O to form inorganic heterojunction. Regarding the way of applying potential to the working electrode during electrodeposition, different methods have been reported so far: potentiostatic [27], cyclic voltammetry as well as pulsed techniques (square wave potential) [19], affecting the final morphology and photoactivity of the TiO$_2$/NTs/Cu$_2$O system. Commonly, within one report, a study of a single electrodeposition mode is presented while the selection of applied potential has never been supported by any preliminary cyclic voltammetry studies. Knowing that the morphology of titania support strongly affects physicochemical and electrochemical properties, comparison between those methods is valuable when the same substrate is used for further Cu$_2$O modification.

Following that, we report on such comparison and the formation of TiO$_2$/NTs/Cu$_2$O composite obtained using the continuous polarization and pulsed modes with different duration of a single pulse. For each deposition method, the optimization procedure was carried out to obtain the most photoactive and stable composite without any protective layer. The set of fabricated materials was characterized by scanning electron microscopy as well as Raman, UV–vis, X-ray diffraction and X-ray photoelectron spectroscopies. Moreover the uniformity studies were undertaken with the support of secondary ion mass spectrometry. The overall performance of anatase nanotubes with embedded Cu$_2$O species was studied under irradiation with linearly changed and constant potential. The complex approach allows for the selection of the most appropriate electrochemical route leading to the highly photoactive p–n heterojunction.

2. Experimental

2.1. Chemicals and materials
Titanium foil (thickness 0.127 mm) used as a substrate material was purchased from Strem. Acetone, ethanol and isopropanol, purchased from POCH, were cleaning agents for the Ti foil prior to the anodization. All the anodization electrolyte components (ethylene glycol and NH$_4$F) as well as copper precursor (CuSO$_4$) for the electrodeposition, lactic acid as a stabilizing agent and Na$_2$SO$_4$ for the electrolyte used for photoelectrochemical measurements were also produced by POCH. Deionized water was obtained using Hydrolab1000 system.

2.2. Nanotubes substrate synthesis
TiO$_2$ anatase nanotubes arrays were synthetized via anodization method. Ti foil of 2 × 3 cm$^2$ was firstly ultrasonically cleaned in acetone, ethanol and deionized (DI) water, followed by drying in air. Afterwards, Ti substrate was immersed in the electrolyte composed of ethylene glycol (85% v/v), DI water (15% v/v) and
0.27 M NH₄F. The electrochemical oxidation took place in two electrode system, where Ti plate served as an anode, while platinum rectangular gauze was used as a cathode. Between those electrodes spaced by 2 cm, the 40 V voltage was applied for 1 h. Both, increase and decrease of voltage were changed gradually by 0.1 V s⁻¹ via software controlled power supply. After the anodization, the as-synthesized nanotubes were rinsed in DI water, then in ethanol and dried in air. The calcination was carried out in the tube furnace (Nabertherm) at the temperature of 450 °C for 2 h. The heating rate was 2 °C min⁻¹.

2.3. Modification procedure of TiO₂ nanotubes with copper oxide

Titania nanotubes were modified by copper oxide using electrodeposition approach in three electrode arrangement. TiO₂NTs were used as a working electrode (WE) while Pt gauze and Ag/AgCl/0.1 M KCl as a counter and reference electrodes, respectively. Autolab PGStat302N (Metrohm Nederland) was used to control the potential and for current registration.

Before electrodeposition, the plate covered by crystalline nanotubes was immersed for 10 min in the electrolyte composed of 0.4 M CuSO₄ and 3 M lactic acid. The pH equalled to 11 was achieved by addition of highly concentrated NaOH solution. pH was controlled by pH-meter. For proper determination of deposition potential, cyclic voltammetry curve was registered for TiO₂NTs immersed in deposition bath (see figure 1).

From the CV shape, two reduction signals localized at −1.0 and −1.5 V versus Ag/AgCl/0.1 M KCl can be observed. According to Bonou et al [30], the reduction process occurs within two stages: Cu²⁺ + e⁻ → Cu⁺ and Cu⁺ + e⁻ → Cu. Therefore, the potential of −1.0 V versus Ag/AgCl/0.1 M KCl was selected for formation of Cu₂O onto TiO₂NTs and thus applied to the working electrode.

The deposition of cuprous oxide was realized via various routes: at the constant polarization and when the WE potential was changed in the pulsed mode with two different lengths of a single pulse. For each route, optimization process was performed and four different samples were fabricated with each approach. The time of the electrodeposition process as well as a pulse length and a number of pulses are listed in table 1. The selection of deposition duration or pulses number was based on the preliminary verification of the photoactivity of fabricated material.

As indicated in table 1, according to the continuous polarization mode, the deposition was carried out for 0.5–3 min. In the case of pulsed mode, one cycle covers application of −1.0 V to the electrode and then 0 V versus Ag/AgCl/0.1 M KCl for the certain time. For long pulses, up to 30 cycles were applied whereas for short pulses mode, the cycles were increased from 15 up to 100. According to the used procedure, samples were labelled as indicated in the last column of table 1. The exemplary electrochemical deposition profiles are
presented in figure 2. After the electrodeposition, samples were rinsed with DI water and dried in 40 °C for 30 min in the argon atmosphere.

2.4. Characterization techniques

The pristine and all modified TiO₂ nanotubes arrays were characterized by scanning electron microscopy (SEM), UV–vis spectroscopy and Raman spectroscopy.

SEM images were recorded by means of FEI Quanta FEG 250 microscope with accelerating voltage kept at 20 kV. The elemental composition of the samples was revealed using energy dispersive X-ray detector(EDX) that is coupled with scanning electron microscope. To confirm uniformity of the copper oxide over the TiO₂NTs substrate, EDX inspection was carried out in three different places and the average values of Ti/Cu atomic % are delivered.

The UV–vis reflectance spectra were measured using a dual beam UV–vis spectrophotometer (Lambda 35, PerkinElmer) equipped with diffuse reflectance accessory. The range of the registered spectra was 300–900 nm and the scanning speed was 60 nm min⁻¹. The transformation of Kubelka-Munk function (KM⁰.⁵Eₚḥ⁰.⁵) against photon energy (Eₚḥ) was plotted to estimate energy bandgap (Ebg). The Kubelka-Munk function was calculated using the relation:

\[ KM = \frac{(1 - R)^2}{2R} \]  

where R is reflected radiation intensity.

The Raman spectra were recorded using confocal micro-Raman spectrometer (InVia, Renishaw) equipped with argon ion laser of the radiation wavelength of 514 nm as an excitation source. The measurements were carried out at 5% of the laser’s total power (50 mW) with an objective ×50.

The presence of crystalline phases in all the fabricated heterojunctions was studied using an X-ray diffraction (XRD) method by means of Bruker D2 Phaser diffractometer with Cu Kα radiation. The XRD measurements were conducted at room temperature and data was collected at 2Θ from 10 to 100° with over 30 min of scan time.

Basing on the photoelectrochemical response, detailed inspection mode was performed for samples exhibiting the highest photoactivity for each deposition. Thus, materials labelled as TiCu-180-CP, TiCu-8-LP and TiCu-60-SP underwent investigation using secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS).

To follow the elemental composition across the material profile the Time of Flight Secondary Ion Mass Spectrometer (TOF SIMS: ION-TOF GmbH) working in dual beam mode was utilized. Bi⁺ 30 keV ions and Cs⁺ 2 keV ions, both incident at 45° to the surface normal, were used as the analysis and sputter beams. The Cs⁺ sputter beam was rastered over 350 μm × 350 μm, 100 μm × 100 μm part in the centre of the milled crater was analyzed. SurfaceLab 7 software (ION-TOF GmbH) was utilized to analyze the change of intensities of characteristics signals during the sputtering. Listed in here signals: CuCs⁺, CuOCS⁺, TiOCS⁺, TICs⁺, OCs⁺ were selected to verify the uniformity of chemical composition from the surface down to the titanium substrate. The SIMS profiles include changes in signals containing Cs ions since such clusters are less influenced by the
matrix effect. Following that, those profiles reflect the real changes in concentration of Cu, Ti and O in investigated samples. Moreover, the signal attributed to CuCs is one order higher than one assigned to Cu⁺.

Following that, remaining species, namely CuO, TiO₂, Ti, O were also represented by Cs containing clusters.

The XPS analysis was carried out on Escalab 250 Xi spectroscopy (ThermoFisher Scientific, UK). The high-resolution spectra were recorded in Cu2p, Ti2p, O1s and Cls binding energy (BE) range, using 20 eV pass energy and 0.1 eV energy step size. The spectroscopy was equipped with Al Ka source. Charge compensation was controlled through the low-energy electron and low energy Ar⁺ ions emission by means of a flood gun. The Avantage software for spectral deconvolution was provided by the manufacturer. The peak positions were corrected by shifting the X-axis to adventitious carbon (C1s peak at 284.6 eV).

2.5. Photoelectrochemical measurements

The electrochemical and photoelectrochemical activities of the samples were studied using an AutoLab PGStat302N potentionstat-galvanostat system (Metrohm Nederland) in the standard three-electrode assembly. As a working electrode both pure and modified titania nanotubes were used, while Ag/AgCl/0.1 M KCl and Pt gauze were used as reference and counter electrodes, respectively. Before the measurements had started, electrolyte composed of 0.5 M Na₂SO₄ was purged with argon gas for about 40 min to remove dissolved oxygen. During entire measurements, Ar-cushion was kept above the electrolyte. Linear voltammetry curves were registered from −0.4 V to + 1.0 V with 10 mV s⁻¹ scan rate under chopped light irradiation with 5 s long dark and illumination periods. The transient photocurrent measurements were performed at +0.5 V versus Ag/AgCl/0.1 M KCl bias voltage. As the light source the high-pressure 150 W xenon lamp (Osram XBO 150) equipped with an automatic light shutter was used. The irradiation intensity was 100 mW cm⁻² and was calibrated using Si reference cell (Rera). The vis light was obtained by cutting of the solar spectrum by 420 nm optical filter.

3. Results and discussion

3.1. Morphology and composition analysis

Figure 3 shows SEM images of pristine (a) and Cu₂O modified TiO₂NTs, using different electrodeposition methods (b–m). As one can see, the height of TiO₂NTs is c.a. 2.4 μm, their inert diameter equals 105 nm whereas outer diameter reaches 140 nm (figure 3(a), insets). Figures 3(b)–(e) present TiO₂NTs overgrown by copper oxide species deposited using constant electrode polarization. Increasingly more deposited Cu₂O crystals can be noticed around outer rings of tubes as the deposition time increases. The same tendency is observed for pulsed electrodeposition mode with the increased number of cycles, both when the pulse duration equals 6 s (figures 3(f)–(i)) and 0.6 s (figures 3(j)–(m)). Similar morphology was obtained by Wang et al[31], even though different deposition technique was used for electrochemical modification. Additionally, in the insets of figures 3(h) and (i), cubic shape of the Cu₂O crystals can be clearly seen. Interestingly, for all three series of specimens prepared using different electrodeposition approaches, nearly spherical bigger particles appeared when the titania substrate is exposed to the electric potential for the longest time or the largest number of deposition cycles was applied (see figures 3(e), (i), (m)). Their shape for all the mentioned samples is similar, however the size varies: the smallest particles are observed for TiCu-100-SP (c.a. 280 nm in diameter) and the biggest for TiCu-30-30LP (up to c.a. 1.3 μm in diameter). Correspondingly, in accordance to other reports [32–34], obtained Cu₂O particles are of a similar shape when pulsed mode of electrode polarization was applied.

Considering that, as well as the results obtained within this report, it can be concluded that size of the particles is closely related to the parameters of the electrodeposition process, namely deposition time in the case of continuous polarization and the number of cycles for pulsed approach.

In order to determine titanium to copper ratios depending on the deposition conditions, the EDX analysis was carried out in different places over the sample area. In table 2, the average value of the Ti/Cu ratio for each material is given. As could be seen, in the case of heterojunctions fabricated at the constant potential, as the deposition time increases, the copper content grows up. Regarding pulsed deposition techniques, along with increase of pulse number, the relation of Ti to Cu at. % decreases. It should be also underlined that the dispersion of values (standard deviation below 10%) is low indicating uniform deposition of Cu₂O over the whole titania substrate.

3.2. Structure studies

According to Ohsaka [35], in Raman anatase spectrum there are six allowed modes that appear at 144 cm⁻¹, 197 cm⁻¹, 399 cm⁻¹, 513 cm⁻¹, 519 cm⁻¹ and 639 cm⁻¹. As one may see in figure 4, recorded bands for TiO₂NTs correspond well with those typical for anatase phase. Analysing Raman spectra of composite materials, one should take into account the position of Cu₂O active bands [36]. It should be noted that peaks at 154 cm⁻¹...
and 636 cm$^{-1}$ coincide with more intensive modes of anatase located at 144 cm$^{-1}$ and 639 cm$^{-1}$. Therefore, the presence of Cu$_2$O crystals in the samples is only possible to be identified basing on the presence of 109 cm$^{-1}$ and 218 cm$^{-1}$ peaks. In fact, in figure 4 these two modes are clearly noticeable for every Cu$_2$O modified specimen, regardless of the deposition route. According to Tsui et al [34], it can be concluded that the enhancement of intensities of the typical for Cu$_2$O Raman scattering peaks accompanied with the decrease of anatase bands correspond to higher amount of Cu$_2$O overgrowing the TiO$_2$NTs substrate.

**Figure 3.** SEM images of pure TiO$_2$NTs (a), and NTs modified with Cu$_2$O: TiCu-30-CP (b), TiCu-60-CP (c), TiCu-120-CP (d), TiCu-180-CP (e), TiCu-4-LP (f), TiCu-8-LP (g), TiCu-15-LP (h), TiCu-30-LP (i), TiCu-15-SP (j), TiCu-30-SP (k), TiCu-60-SP (l), TiCu-100-SP (m).

**Table 2.** The variation of the atomic Ti/Cu ratios depending on the sample preparation.

| Sample   | Average Ti/Cu atomic ratio [at %] |
|----------|----------------------------------|
| TiO$_2$  | no copper presence               |
| TiCu-30-CP | 59.7/40.3                      |
| TiCu-60-CP | 46.7/53.3                      |
| TiCu-120-CP | 33.3/66.7                      |
| TiCu-180-CP | 20.7/79.3                      |
| TiCu-4-LP   | 61.3/38.7                       |
| TiCu-8-LP   | 54.3/44.3                       |
| TiCu-15-LP  | 30.7/69.3                       |
| TiCu-30-LP  | 12.7/87.3                       |
| TiCu-15-SP  | 75.3/24.7                       |
| TiCu-30-SP  | 63.3/36.7                       |
| TiCu-60-SP  | 49.3/50.7                       |
| TiCu-100-SP | 38.7/61.3                       |
Moreover, to confirm the presence of Cu$_2$O, the XRD analysis was performed for the series of the heterojunctions. In figure 5, XRD patterns are shown and the clear signals typical for anatase and titanium substrate were found. Moreover, independently on the used deposition technique the presence of Cu$_2$O was confirmed. It could be also seen, that when the deposition time or cycles number increases, the intensity of signals assigned to Cu$_2$O grows up.

As it was stated in the experimental section, on the basis of photoelectrochemical activity (discussed in details later on), within each deposition route one sample exhibiting the highest photoresponse was selected for further detailed inspection of the heterojunction to get the information about the chemical nature of copper species using XPS technique and their uniform deposition via SIMS studies.

The high-resolution XPS spectra are presented in figure 6. The spectra were deconvoluted using below presented fitting model in order to determine the differences in surface chemistry between various approaches of Cu$_2$O electrochemical deposition method. The deconvolution results are summarized in table 3. The successful deposition of Cu$_2$O was confirmed through XPS spectra recorded at BE (binding energy) range of Cu2p (figure 6(a)), which revealed a strong component, with Cu2p$_{3/2}$ peak at 932.4 eV. This component is ascribed in numerous reports to Cu$_2$O [37–40], and while it might have originated from metallic Cu, the weak satellite feature observed between 944 and 947 eV (also in the inset of figure 6(a)) testifies for dominant Cu$_2$O presence [37]. Thus, the obtained results prove that applied electrochemical conditions lead to the formation of the desirable copper oxidation state, since compared to CuO, Cu$_2$O is characterized by the narrow bandgap which is suitable for energy harvesting in the visible range and positions of energy bands that corresponds to those of TiO$_2$ [41].

The second, minor component was noted at BE shifted by + 2.0 eV, which might originate from the presence of carbonates or dihydroxides resulting from oxidation in air [42]. This component was only noted for TiCu-8-LP and TiCu-60-SP samples while its share in total copper content was low and equal to 4% and 8%, respectively.
Next, the spectra deconvoluted within Ti\textsubscript{2p\textsubscript{3}}/2 BE range (see figure 6(b)) revealed a single chemical state of titanium, with peak energy at 459.2 eV characteristic for TiO\textsubscript{2} anatase \[43–48\]. The total contribution from titanium oxides may provide information regarding thickness of deposited Cu\textsubscript{2}O film, where the smallest share of Ti (4.2 at\%) for TiCu-180-CP might be correlated with the highest thickness with respect to thinner copper oxide layers in the case of TiCu-8-LP and TiCu-60-SP samples (7.3\% and 9.6\%, respectively). Following that, different enhancement in photocurrent may be expected depending on deposition route. There was no sign of titanium at lower oxidation states on the recorded spectra that proves complete and tight coverage of Ti substrate by the inorganic heterojunction.

The O\textsubscript{1s} spectra, presented in figure 6(c), corroborates previously obtained results, with the dominant component located at ca. 530.2 eV corresponding to oxygen in crystal lattice of Cu\textsubscript{2}O and to some extent TiO\textsubscript{2}. The second peak present at higher binding energies should be ascribed to non-lattice oxygen O* and hydroxyl bonds, but can also originate from adventitious carbon layer adsorbed on the surface during air exposure of the electrodes.

To summarize, the Cu\textsuperscript{2+}-to-O\textsuperscript{2-} ratio was the highest for TiCu-180-CP material (1.45:1), with lack of notable contribution from higher oxidation states of copper and the smallest contribution from non-lattice oxygen. The oxides formed using proposed approach indicates significant contribution of hydroxyl species but also slight modification of the chemistry of TiO\textsubscript{2} substrate. Concluding, continuous polarization mode allows for fabrication of purely Cu\textsubscript{2}O phase whereas when short pulses were applied some small contribution of CuO could impact the material photoactivity.

Moreover, to denounce the copper surface chemistry an analysis of the peak shift between Cu\textsubscript{2}O and metallic Cu Auger Cu LMM spectra has been carried out. The Augers spectroscopy measurements were performed for three samples that exhibit the highest photoactivity (as reported later on) within each deposition route. The recorded Cu LMM spectra are shown in figure 7. The peak of each of these samples lies in the kinetic energy range characteristic for Cu\textsubscript{2}O interaction — 916.8 eV \[49–51\]. The obtained values are: 916.7 eV for sample TiCu-60-SP, 916.8 eV for TiCu-8-LP and 917.1 eV for sample TiCu-180-CP. Therefore, it can be stated that
obtained results excluded certainly the presence of CuO and Cu species in the samples and are in accordance with XRD results.

SIMS depth profiles were recorded to determine the penetration depth of the copper oxide species into the titania nanotube porous layer and its dependence on the electrochemical approach used for TiO$_2$NTs modification. As shown in figure 8, different ions were detected for three TiCu samples selected on the basis of photoelectrochemical activity. In order to minimize the matrix effect Cesium clusters with fragments characteristic for the main components of layers were traced. The SIMS analysis shows the variation of different Cs-containing ions characteristic for: i) copper oxide, ii) titanium dioxide NTs and iii) Ti plate. Apart from a little signal variation close to the surface (c.a. first 100 s), that is related to the interaction of ions with the most external part of the sample, signals attributed to ions containing Cu, CuO, TiO and O species are on the same level till 4.5 ks. As the sputtering time pass, the signals assigned to all these ions become parallel to each other. It demonstrates highly uniform deposition of copper oxide species along titania nanotubes from the surface down to their bottom. When the sputtering time exceeds c.a. 5 ks, the intensity of those signals falls sharply whereas gradual increase of TiCs$^+$ ions indicates that Ti metal substrate has been reached. It proves also very narrow height distribution of the nanotubes. The simultaneous decrease of all signals attributed to Cu, CuO, TiO and O containing species indicates that irrespectively of the deposition mode, the uniform inorganic-inorganic heterojunction was fabricated.

### 3.3. Optical properties

The values of gaps between the conduction and the valence bands for the reference (bare) TiO$_2$NTs and TiO$_2$NTs modified with Cu$_2$O were determined in order to define their electronic structures and the correlation between energy bandgap and particular deposition approach. According to the equation (1), the values of Kubelka-Munk functions were obtained from the recorded reflectance spectra (figures 9(a), (c), (e)), which were subsequently converted into Tauc plots (see figures 9(b), (d), (f)). Basing on the intersection of tangent with the energy axis, the bandgaps for allowed transitions were determined as indicated in each Tauc plot.

For all investigated TiO$_2$NTs samples, the strong absorbance in UV range is observed that is typical for titania materials. However, in the spectrum of unmodified material one can see an enhanced absorbance within the range of 380–550 nm. It can be attributed to the geometrical features of nanotubes, i.e. the light undergoes multiple reflection inside the nanotube and constructive interference enhances the registered signal, as it was presented in the work of Gong et al.\cite{52}.

Main reflection bands for all the Cu$_2$O modified specimens are red-shifted, comparing to the reference TiO$_2$NTs sample. According to Wang et al.\cite{53}, the reduction of the energy necessary for the transition is attributed to the insertion of 3d states of the metal in the conduction band of TiO$_2$. On the contrary to the unmodified TiO$_2$, after Cu$_2$O loading the absorbance within 380–550 nm range diminishes that results from the change in the geometrical dimensions, namely decrease of the internal diameter due to copper oxide deposition. Moreover, it is thought to be the result of the uniform Cu$_2$O loading (correspondingly to the SIMS results, figure 8) as well as deep interaction between TiO$_2$ nanotubes and Cu$_2$O nanoparticles, similarly as in the work of Jagminas et al.\cite{54}.
Analysis of Tauc plots (figures 9(b), (d), (f)) draws the observation that the $E_{bg}$ characteristic for anatase ($\sim 3.18$ eV) shifts towards the visible region for all the prepared TiO$_2$-Cu$_2$O heterostructures. Following the literature [54], up to two absorption edge values were determined for each specimen. In table 4 the values of energy bandgaps corresponding to the absorption edges for the series of TiO$_2$-Cu$_2$O samples are presented. Both the red-shift and the enhanced light absorption in the visible region above 550 nm are the consequence of homogenous distribution of copper oxide species and energy coupling between both parts of the heterojunction [54]. Taking into account the significant decrease of energy bandgap found for the copper oxide modified titania, improved photoelectrochemical activity could be expected for TiO$_2$-Cu$_2$O comparing to the pristine TiO$_2$NTs.

3.4. Electrochemical characterization
All the fabricated materials were characterized using linear voltammetry (LV) and chronoamperometry (CA) when the working electrode was exposed to simulated solar visible light illumination alternating on and off every
10 s. Figures 10(a), (b) and (c) present the effect of the applied potential on the photocurrent density enhancement, using LV within $-0.4$ and $+1.0$ V versus Ag/AgCl/0.1 M KCl range. As one may see, the dark current for every measured sample, except for TiCu-180-CP, is near to zero and can be neglected. For reference sample, namely pristine TiO$_2$NTs, both LV (figure 10(a)) and CA (figure 10(b)) runs prove negligible activity under visible irradiation resulting from its wide bandgap energy. When pristine TiO$_2$ was irradiated, the photocurrent reaches only 2.5 $\mu$A cm$^{-2}$ (see also figure 11(b)). In the case of modified titania the substantial increase in photocurrent density can be observed upon exposure to light, especially when the bias potential exceeds $+0.2$ V. It is noteworthy, that TiCu-120-CP, TiCu-8-LP and TiCu-30-LP samples demonstrate strong anodic peak around $+0.1$ V versus Ag/AgCl/0.1 M KCl. Such rapid spikes in anodic regions of voltammograms occur due to the rapid oxidation process in the electrode material [55]. It is thought [56] to be an evidence of oxidation of Cu$_2$O to CuO in the material, probably resulting from its instability within this potential region. It is also possible that the local increase of the current density is determined by an exceptionally high separation of photogenerated electron-hole pairs [57]. Holes diffuse to the surface of the semiconductor where they are trapped by reduced species in the electrolyte, while electrons go to the back contact and are collected in the external circuit. Similar behaviour was observed by Ye et al [58].
Table 4. Values of energy bandgaps determined on the basis of Tauc plots presented in figure 9. (N—not determined).

| Sample       | Absorption edge/eV |
|--------------|---------------------|
| TiO₂NTs      | 3.18                |
| TiCu-30-CP   | 2.25                |
| TiCu-60-CP   | 2.08                |
| TiCu-120-CP  | 2.04                |
| TiCu-180CP   | 1.83                |
| TiCu-4-LP    | 2.28                |
| TiCu-8-LP    | 2.10                |
| TiCu-15-LP   | 2.07                |
| TiCu-30-LP   | 1.20                |
| TiCu-15-SP   | 2.60                |
| TiCu-30-SP   | 2.42                |
| TiCu-60-SP   | 2.13                |
| TiCu-100-SP  | 1.72                |

Absorption edge/eV values for different samples.
For several samples (TiCu-180-CP, TiCu-120-CP, TiCu-30-CP, TiCu-15-LP, TiCu-30-LP, TiCu-15-SP) the photocurrent density saturates at +0.2 V and for TiCu-180-CP it was 230 times higher than for bare TiO₂NTs. Comparing to other electrochemically obtained Cu₂O-TiO₂ heterostructures, it is the first such a significant current density enhancement for this type of material. Similarly, investigating the transient photocurrent response over time of 5 min, under several cycles of on-off visible solar illumination at an applied potential of +0.5 V versus Ag/AgCl/0.1 M KCl (see figures 10(b), (d), (f)), an enormous photocurrent density enhancement can be noticed. Defining the enhancement factor (Eₜ) as a ratio between photocurrents of Cu₂O-TiO₂ composite and bare titania substrate, the Eₜ for all the obtained materials were calculated and collected in table 5. As one can see, Eₜ reaches the value of 14 up to 230 for TiCu-60-CP and TiCu-180-CP, respectively.

In order to compare photoactivity of fabricated heterojunctions to the response of other electrochemically synthesized Cu₂O-TiO₂ heterojunctions, the list of Eₜ values has been presented in table 6. As can be observed, after Cu₂O deposition the enhancement for reported elsewhere materials does not exceed 50, that makes achieved here results very attractive since such Eₜ has not been reached up till now.

Moreover, it clearly demonstrates that the deposition of Cu₂O nanoparticles refined the separation between photogenerated electrons and holes at the heterojunction, mostly as a result of widened range of absorbed
wavelength, which corresponds to the bandgap shift for Cu$_2$O modified samples (see figure 9). When the solar radiation was shadowed, a negligible current was registered, while, when the light fell on the sample, the photocurrent density returned almost immediately to its original value. It proves an excellent sensitivity to the illumination and solar-to-electrical energy conversion ability. This feature can be found for all the tested samples. Depending on the material, different level of reproducibility was achieved. During 5 min long measurement, the photocurrent density tended to decrease for TiCu-30-CP, TiCu-4-LP, TiCu-8-LP, TiCu-30-LP, TiCu-30-SP and TiCu-60-SP. These can demonstrate high recombination rate of photogenerated charge.

Table 5. The values of the enhancement factor determined for obtained samples.

| sample       | $E_f$ | sample       | $E_f$ | sample       | $E_f$ |
|--------------|-------|--------------|-------|--------------|-------|
| TiCu-30-CP   | 68    | TiCu-4-LP    | 71    | TiCu-15-SP   | 47    |
| TiCu-60-CP   | 14    | TiCu-8-LP    | 113   | TiCu-30-SP   | 71    |
| TiCu-120-CP  | 116   | TiCu-15-LP   | 103   | TiCu-60-SP   | 87    |
| TiCu-180-CP  | 230   | TiCu-30-LP   | 79    | TiCu-60-SP   | 87    |

Table 6. The photoactivity (quantified as $E_f$) for already reported Cu$_2$O-TiO$_2$NTs heterojunctions obtained using electrochemical techniques.

| Electrochemical technique used for Cu$_2$O deposition onto TiO$_2$NTs substrate | $E_f$ under vis irradiation | Reference |
|--------------------------------------------------------------------------------|----------------------------|-----------|
| square wave voltammetry                                                       | 1.45–2                     | [59]      |
| pulsed electrodeposition followed by potentiostatic anodization                | 5                          | [60]      |
| potentiostatic mode                                                            | 20                         | [33]      |
| potentiostatic mode                                                            | 2.42                       | [61]      |
| 3-step pulses plating                                                          | 2.5                        | [34]      |
| potentiostatic deposition                                                      | 35                         | [62]      |
| square wave voltammetry route                                                  | 7.8                        | [63]      |
| potentiostatic depositions                                                     | 50                         | [64]      |

Figure 11. Transient photocurrent recorded for TiO$_2$NTs, TiCu-180-CP, TiCu-8-LP and TiCu-60-SP both under UV–vis and only vis irradiation in 0.5 M Na$_2$SO$_4$ electrolyte.
carriers. The photocurrent density remains stable for TiCu-180-CP, TiCu-120-CP and TiCu-60-CP, while for TiCu-15-LP, TiCu-60-LP and TiCu-100-LP it continues to increase. Notably, for every deposition mode, there was an optimal deposition time or number of cycles for certain pulse length, which allowed to obtain the highest photocurrent density enhancement within each set. For constant polarization mode time equalled to 180 \text{s} (TiCu-180-CP), for pulsed mode with long pulses the best photocurrent density enhancement was found to be achieved with 8 cycles and for short pulses—for 60 cycles. Therefore, for detailed structure inspection using SIMS and XPS techniques those three composites were selected.

As one can see, table 5, the highest photocurrent density under visible illumination was achieved for the sample TiCu-180-CP. The explanation of this phenomenon might be as follows \cite{65}: while an applied potential corresponds to the reduction: Cu$^{2+}$ $\rightarrow$ Cu$^{+}$, the formation of Cu$_2$O layer occurs on the working electrode, whereas near to zero potential, the oxidation of Cu$_2$O takes place, which involves some dissolution of material. Apparently, a partial periodic dissolution of Cu$_2$O influences negatively the photoactivity of the layer, probably due to the formation of residual CuO species as indicated by XPS analysis. Those CuO inclusions act as defects and thus deaccelerate the charge carriers transport.

For further electrochemical investigations, out of every set of materials prepared via various deposition modes, one sample was chosen, basing on the best performance. For these three samples, i.e. TiCu-180-CP, TiCu-8-LP and TiCu-60-SP, as well as for the pristine TiO$_2$NTs, chronoamperometric measurements in UV–vis light and in the presence of CO$_2$ were performed.

In order to compare the performance of the TiO$_2$–Cu$_2$O hybrid in visible and UV–vis light, the chronoamperometric measurements were recorded and presented in figure 11. Except for TiCu-60-SP, all the samples occurred to be stable over 5 min i.e. along the whole illumination period. Comparing their photocurrent density, one may notice, that this value recorded in the visible light for bare TiO$_2$NTs is around 50 times smaller than the one obtained under UV–vis illumination. Such behaviour is attributed to the bandgap energy of pure titania that corresponds to the ultraviolet range. Conversely, all the samples overgrown by Cu$_2$O species reveal significantly higher photocurrent density upon the visible light illumination than if the whole solar spectrum irradiates the composite electrode.

This phenomenon may result from the energy band alignment of both parts of the heterojunction and the charge transport between both elements, as indicated in figure 12. When the electrode is exposed to the full solar spectrum in both parts electron-hole pairs are photogenerated. Then, electrons generated both conduction bands are transferred to the collecting Ti substrate, whereas holes moves to the opposite direction towards electrode/electro-lyte interface. Those holes could then be involved in water oxidation. However, holes generated in the valence band of Cu$_2$O may also recombine with electrons from the conduction band of TiO$_2$ (assigned as R in figure 12) leading to the lower amount of charge collected at the Ti substrate.

However, when only visible light illuminates the working electrode, Cu$_2$O layer is an exclusive zone, in which excitons are photogenerated. Proposed justification is supported by the band gap value of bare TiO$_2$NTs corresponding to only UV region and Cu$_2$O-modified samples (see paragraph 3.3), for which two absorption edges shifted towards visible range were found. Moreover, the difference in photostability between those samples were found under UV–vis and only vis irradiation. The explanation of such phenomenon could be

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure_12.png}
\caption{The scheme of energy depicting the mechanism for the improved photoelectrochemical activity of TiO$_2$NTs-Cu$_2$O hybrid under visible (right) and UV–vis light (left) illumination (CB—conduction band, VB—valence band, R—recombination).}
\end{figure}
related with some photodegradation of the copper oxide film as indicated by Tsui et al.\footnote{34} According to their results, the application of intense light radiation, e.g. laser beam, may lead to photodissolution process reducing the particle size. However, for samples fabricated via pulsed mode, the current value under visible radiation, but in our case generated by solar simulator equipped with xenon lamp as a light source, is stable proving their satisfactory photostability. On the contrary, for TiCu-180-CP material recorded photocurrent decreases gradually. Nevertheless, when electrode was irradiated by the full solar spectrum, photocurrent diminution occurs for the heterojunctions obtained via pulsed mode reaching the highest drop for TiCu-60-SP. In those conditions, the run of transient photocurrent for TiCu-180-CP material is the most stable. Such behaviour demonstrates that deposition route impacts not only the value of achieved photoconversion rate but also its preservation under particular light spectrum focused onto the electrode surface.

For some preliminary studies of the photodegradation, SEM inspection was undertaken\footnotemark[13] and reveals that some changes in morphology occurs. As can be observed, the formation of flake-like structures takes place, less or more dense when simultaneous electrode polarization occurs. As was concluded by Tsui et al,\footnote{33, 62, 64, 66, 67} illumination may lead to rearrangement of Cu$_2$O to expose the more stable facets. Following that, many investigations on photoelectrical properties of Cu$_2$O focus on its performance upon the exposure to only visible light or deposition of some protective layer when the full solar spectrum is applied\footnote{68}. However, as was identified, photodegradation is much more complex since deposition route and radiation spectrum significantly affect photoconversion stability and needs further inspection.

4. Conclusions

Herein, we presented the optimized approach enabling for formation of highly uniform heterojunction composed of highly ordered titania nanotubes modified by copper (I) oxide species. The deposition was realized in three different electrochemical modes covering constant polarization and pulsed one with two different pulse duration 6 s and 0.6 s. Within each route, time or cycle number was optimized to reach the highest possible enhancement of the recorded transient photocurrent under electrode irradiation. Detailed SEM inspection revealed that copper oxide species of nanometers dimensions overgrown tightly TiO$_2$ walls and penetrate tubular layer from the surface down to the titania base. For prolonged synthesis procedure, some agglomerates were obtained that block completely titania pores. XPS studies indicated formation of purely copper (I) phase for constant polarization approach whereas for pulsed mode some little amounts of CuO species were found. Raman spectra together with XRD patterns recorded for the composites show bands typical for anatase crystalline phase of titania support and Cu$_2$O. Photoelectrochemical characterization covering registration of photocurrent using linear voltammetry and chronoamperometry allowed to indicate deposition parameters leading to the most photoactive electrode within each fabrication method. The results point to the fact that 180 s is sufficient in the case of potentiostatic polarization whereas for 6 s long pulses—8 cycles and for 0.6 s long pulses—80 cycles should be applied. Among those, TiO$_2$-Cu$_2$O composite obtained via constant polarization exhibited 230 times higher photocurrent value under vis and 3.8 under UV–vis radiation comparing to bare titania when $+0.5$ V bias voltage was applied. Such superior light harvesting results from the widened absorbance due to the presence Cu$_2$O layer and band alignment between both elements of formed junction.
enabling charge transport to the Ti collector. Moreover, the variation in photostability depending on the deposition technique and radiation spectrum was found and at a first glance related with morphology rearrangement.

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