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Fabrication of a UV Photodetector Based on \(n\text{-TiO}_2/p\text{-CuMnO}_2\) Heterostructures

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Abstract: The heterojunction based on \(n\text{-TiO}_2\) nanolayer/\(p\text{-CuMnO}_2\) thin film was achieved using an efficient two-step synthesis process for the fabrication of a UV photodetector. The first step consisted of obtaining the \(\text{TiO}_2\) nanolayer, which was grown on titan foil by thermal oxidation (Ti-TiO\(_2\)). The second step consisted of \(\text{CuMnO}_2\) thin film deposition onto the surface of Ti-TiO\(_2\) using the Doctor Blade method. Techniques such as X-ray diffraction, UV-VIS analysis, SEM, and AFM morphologies were used for the investigation of the structural and morphological characteristics of the as-synthesized heterostructures. The Mott–Schottky analysis was performed in order to prove the \(n\text{-TiO}_2/p\text{-CuMnO}_2\) junction. The \(I-V\) measurements of the \(n\text{-TiO}_2\) nanolayer/\(p\text{-CuMnO}_2\) thin film heterostructure confirm its diode characteristics under dark state, UV and visible illumination conditions. The obtained heterojunction, which is based on two types of semiconductors with different energy band structures, improves the separating results of charges, which is very important for high-performance UV photodetectors.

Keywords: heterojunction; UV photodetector; \(\text{TiO}_2\text{-CuMnO}_2\)

1. Introduction

Recently, UV sensors/photodetectors have drawn growing attention due to their wide applications in environmental safety, biological research, medicine, gas sensors, optical communication, astronomical studies, space exploration, and so forth [1]. Lately, sensory technology has evolved and is constantly growing to improve the quality of life and environmental protection. Hence, ZnO [2], TiO\(_2\) [3], CuO/Cu\(_2\)O [4], SnO/SnO\(_2\) [5], and VO\(_2\)/V\(_2\)O\(_5\) [6] are some examples of metal oxides and have been extensively studied for use as high-performance UV photodetectors [7]. These types of materials can have different structures, from nanowires to nanospheres, which have a direct influence on their performance in detection applications. The literature data present that some characteristics, such as composition, crystal quality, morphology, particle size and distribution, surface area, porosity, and bandwidth have influenced the performances of the catalysts’ photoactivity [8].

Among the different metal oxides, TiO\(_2\) is one of the most studied semiconductors because of its interesting properties and promising applications in solar cells [9], gas sensors [10], pharmaceutical applications [11], photocatalysis [12], batteries [13], and UV detectors [14]. UV detectors can be used in a wide range of detection applications, such
as emitter calibration, satellite communications, chemical and biological analyses, flame detection and astronomical studies [15]. Recently, TiO$_2$, which is considered to be highly photoactive and stable under UV irradiation due to its band gap, has been applied to the most commonly used UV sensors. In terms of synthesis, TiO$_2$ UV photodetectors can be fabricated by many methods such as sol-gel, thermal hydrolysis, thermal decomposition, micro-emulsion, chemical vapor deposition (CVD), potentiostatic anodization or radio-frequency magnetron sputtering techniques [16]. Many researchers have focused on the coupling of semiconductor materials, based on their unique properties, namely that two types of semiconductors with different energy band structures can improve the separating results of charges. The heterojunction of TiO$_2$ with numerous semiconductors, including CdTe [17], CuI [18], Cu$_2$O [19], MoS$_2$ [20], and ZnO [21], was studied and an enhancement in both the photoelectrochemical properties and the photovoltaic or photocatalytic performance was observed.

Lately, the oxides CuMO$_2$ (M = Al, Ga, Fe, Mn, Cr) have attracted researchers’ attention because of their wide band gaps and fast-hole diffusion coefficients. These binary metal oxides have been vastly used in many areas, including the production of hydrogen, storage of oxygen, water splitting, supercapacitors, and sensors. Shi et al. have obtained a CuGaO$_2$ film that was deposited on a β-Ga$_2$O$_3$ substrate by using a reactive deposition epitaxy technique. The results that were achieved allowed them to more efficiently design a β-Ga$_2$O$_3$-based wide band gap-oxide heterojunction for advanced UV applications [22]. Ahmadi et al., by using the sputtering deposition method, have developed a heterojunction of thin films comprised of Al-doped ZnO and (Mg, N)-doped CuCrO$_2$. These materials have a wide band gap that makes them transparent in visible light but also good UV-absorbers [23]. Dursun et al. have prepared CuCrO$_2$ nanoparticle-decorated SnO$_2$ nanofiber composites as novel p-n heterostructured semiconductor photocatalysts for the degradation of organic pollutants in wastewater [24].

Based on the literature data, all photodetectors are made of nanostructures that are more promising for manufacturing and practical applications compared to simple thin p-n films [23]. Until now, CuMnO$_2$ films have been obtained by different deposition methods such as sol-gel, wet chemical, precipitation, gas phase, evaporation decomposition, and laser ablation. Velmurugan et al. described a visible light-active SnO$_2$/CuMnO$_2$ p-n heterojunction, which was successfully applied to the Tetracycline photoelectrochemical detection [25]. In addition, Lazau et al. presented a new “n-p” TiO$_2$-CuMnO$_2$ heterojunction synthesized for the first time, following three synthesis steps for layer-by-layer deposition [26].

Some major parameters are very important for practical applications; photodetectors should have a high detectivity, a good response speed and a high stability. To that point, some recent studies are listed: Tsai et al. demonstrated photocurrent-to-dark-current ratios and the fast response of photodiodes that were based on p-Cu$_2$O/n-TiO$_2$ nanostructures [27]; Wang et al. used N-doped TiO$_2$/C heterojunctions in order to increase the absorption of the visible light region and the photocatalytic activity [28]; Chang et al. investigated the heterojunction effects of the grown TiO$_2$ nanotubes on the photodiode characteristics by atomic layer deposition (ALD) [29,30]. The heterojunctions that combine TiO$_2$ NTs with SnO$_2$ [31], NiO [32], or CdS [33] have been widely used to improve the performance of UV photodetectors [34]; cuprous sulfide (Cu$_2$S) is an n-type semiconductor often used for visible light-sensitive photodetector fabrication [35].

This study reports a new strategy for developing a UV photodetector that is based on the heterojunction between n-type TiO$_2$ and p-type CuMnO$_2$. Compared to our previous studies [26], the progress and advantages of this study are related to the reduction of the time and number of synthesis steps needed to obtain the heterostructure (Ti-TiO$_2$-CuMnO$_2$), as well as the removal of the risks which could occur during the fabrication process of the Au films (defoliation from the glass support) and TiO$_2$ films (poor adhesion on Au film) for sensor development.
2. Materials and Methods

2.1. Reagents

All synthesis reagents were used without any treatment, as follows: titanium foil (99.99% purity), hydrofluoric acid (HF) solution (0.5 M), α-terpinol ethyl cellulose, acetone and ethyl alcohol. The CuMnO₂ powder was synthesized by the ultrasound-assisted co-precipitation method, which used the nitrate precursors [Cu(NO₃)₂·3H₂O and Mn(NO₃)₂·4H₂O] in a NaOH solution, a synthesis time of about 40 min, and 80% ultrasound amplitude [36].

2.2. Fabrication of the Sensors Based on the “n-p” Type Heterojunction Ti-TiO₂-CuMnO₂

The Ti-TiO₂-CuMnO₂ heterostructure of the sensor was achieved in two steps (Figure 1). The first step consisted of obtaining the TiO₂ layers that were grown on Ti foil (with an effective area of 1 cm²) by thermal oxidation (Ti-TiO₂), as follows: prior to the chemical treatment, the Ti foil was degreased in an ultrasonic bath in acetone and ethyl alcohol solutions; the Ti foil was then etched in an HF solution (0.5 M) for different periods of time (1 h, 2 h, 3 h) at room temperature. After the chemical process, the titanium foils were washed with distilled water, then air-dried. For the formation of crystalline TiO₂, the process of thermal oxidation was carried out in a tubular furnace in a controlled atmosphere consisting of a mixed gas flow of Ar and O₂ at a temperature of 500 °C for 4 h. The second step consisted of depositing the CuMnO₂ film onto the surface of the Ti-TiO₂ layers by using the Doctor Blade method. Thus, for the deposition of the CuMnO₂ film, a homogeneous paste was prepared as previously described in our paper [26]. The Ti-TiO₂-CuMnO₂ heterostructures were then air-dried for 30 min, and calcinated at 250 °C for 1 h. Before and after deposition, the films were UV cleaned using the UV Ozone Cleaner and then deposited in hermetically sealed dishes. In order to facilitate data collection, gold wires were affixed to the Ti and p-CuMnO₂ films by using Ag paste. Table 1 presents the sample codes and synthesis conditions.

Table 1. The sample codes according to the synthesis conditions.

| Sample       | Codes | Etching (Ti Foil) Cᵥ[H₃(M)/t(h)] | Oxidation Tᵦ[C°/t(h)] | Sensor Type               | Codes | Thermal Treatment T₁°[C°/t(h)] |
|--------------|-------|----------------------------------|-----------------------|---------------------------|-------|-------------------------------|
| Ti-TiO₂      | S1    | 0.5                              | 1                     | Ti-TiO₂-                  | S1a   | 250/1                         |
|              | S2    |                                  | 2                     | CuMnO₂                   | S2a   |                               |
|              | S3    |                                  | 3                     |                          | S3a   |                               |

Figure 1. Fabrication process of the sensors.
2.3. Materials Characterization

The crystalline structure of the as-synthesized samples was characterized by X-ray diffraction (XRD, PANalytical X’Pert PRO MPD Diffractometer, Almelo, The Netherlands) with Cu-Kα radiation (\(\lambda = 1.5418\text{Å}\)) in the range \(2\theta = 10–80^\circ\). The morphology of the layers and heterostructures was examined using scanning electron microscopy (SEM, FEI Inspect S model, Eindhoven, The Netherlands). The morphologies of the as-synthesized sensors were investigated by atomic force microscopy (AFM, Model Nanosurf® EasyScan 2 Advanced Research, Liestal, Switzerland), using the non-contact mode (scan size of 1 \(\mu\text{m} \times 1 \mu\text{m}\)).

The optical properties of all of the samples were recorded using the UV-VIS analysis (PerkinElmer Lambda 950 UV/Vis spectrophotometer, Connecticut, USA) with an integrating sphere, in the range of 300–800 nm. The band gap \(E_g\) of the semiconductor materials was determined by plotting the Kubelka–Munk function against energy (eV). For electrochemical measurements, a Voltalab Potentiostat model PGZ 402 (Wuhan Corrtest Instruments Corp., Wuhan, China) was used with a three-electrode cell system comprised of an Ag/AgCl/KCl saturate electrode (reference electrode), a platinum wire (counter electrode) and Ti-TiO\(_2\) layers, and CuMnO\(_2\) film (working electrodes) in 10\(^{-1}\) mol/L Na\(_2\)SO\(_4\) aqueous solutions. The potential range was established at −0.8–0.6 V for the Ti-TiO\(_2\) layers, and 0.2–1.1 V for the CuMnO\(_2\) film, respectively, with a 25 mV potential step.

The electric properties of the obtained UV photodetectors were measured using the Keithley 2450 SourceMeter SMU Instrument (Keithley Company, Cleveland, OH, USA). The parameter of current-voltage (I-V) demonstrates the \(n\)-TiO\(_2\)/p-CuMnO\(_2\) heterojunction behavior in dark state, UV and Vis illuminated conditions. The measurements were recorded in forward bias with “−” at the “n” area (99.99% Ti electrode) and “+” on the gold wire placed on the p-type CuMnO\(_2\) semiconductor film. The applied voltage varied over ranges between −2 V and 2 V with a step rate of 10 mV/s. The UV detection characteristics were evaluated by a current-time measurement at a bias of 2 V under 20 s of lamp illumination at \(\lambda = 365\) nm with a light power of 0.1 mW/cm\(^2\). For visible irradiation, a Vis lamp at a wavelength range of 450–700 nm with a light power of 0.2 mW/cm\(^2\) was used. A Solar 4000 Sensor (AMPROBE) (Octopart Inc., New York, NY, USA) device was used to calibrate the light power of the UV and Vis lamps that were used for the opto-electrical measurements.

3. Results and Discussion

3.1. Structural and Morphological Characteristics

Figure 2 shows the crystalline structure by XRD of the Ti-TiO\(_2\) layers and the as-synthesized Ti-TiO\(_2\)-CuMnO\(_2\) heterostructures at different etching times. The presented results show that the thermal oxidation of the Ti foil at 500 °C conducted to the rutile phase transition (JCPDS 01-075-1010), which was confirmed by the main peaks at \(2\theta\): 27.65°, 32.47°, 54.64° (Figure 2a). In addition, the average crystallite sizes of the as-prepared Ti-TiO\(_2\) layers were estimated, using the Debye–Scherrer formula, to be about 62 nm (S1), 40 nm (S2) and 30 nm (S3). It is likely that the subsequent restriction in particle growth can be attributed to the decrease in the diffusion rate of titanium, which is responsible for the reaction speed. The XRD pattern of pristine CuMnO\(_2\) that was previously reported in our paper [26] indicates that the sample crystalized in the crednerite form (JCPDS 00-014-0623) is also confirmed by peaks at \(2\theta\): 31.32°, 33.45°, 37.0°, 52.42°, 56.85°.
The XRD patterns of the as-synthesized heterostructures S1a, S2a and S3a presented in Figure 2b show that the diffraction peaks specific for CuMnO2 (crednerite form) and TiO2 (rutile form) are preserved, which demonstrates the good deposition of the CuMnO2 films onto the Ti-TiO2 layers.

Figure 3 shows the surface morphology of the oxidized titanium samples S1 (Figure 3a), S2 (Figure 3b), and S3 (Figure 3c) for the Ti-TiO2 layers. The SEM images show that the passivation layer from the surface of Ti foil was completely removed for all three of the samples. TiO2 layers were grown in the polyhedron form with curved surfaces (broken stone appearance). The growing of the TiO2 layer was oriented in clearly defined and delimited directions by the curved surfaces of the polyhedral structure. The TiO2 layers were very well defined, and the sample that was etched for 3 h (S3a) showed a compact growth of elongated grains. The distance between the elongated rows of grains decreased with the increase of corrosion time, and at 3 h the rows of grains were joined over the entire surface of the layer (Figure 3c). The CuMnO2 films were uniformly deposited, without cracks, and were covering the entire TiO2 layer surface following its polyhedral shape, as can be seen in Figure 3d–f.

Figure 4 shows the 2D (Figure 4a–c) and 3D (Figure 4d–f) surface morphologies by AFM analysis for the Ti-TiO2 layers, which confirms the results that were obtained by the related SEM images, which indicated that TiO2 particles have an oriented growth. The Nanosurf EasyScan 2 software was used for the determination of the particle sizes from the surface (Figure 5).

In addition, the surface roughness (measured surface area of about 1.326 pm$^2$), which is represented by the average roughness $S_a$ and the mean square root roughness $S_q$, and the layer thickness were determined from the AFM analysis data. The topographical parameters $S_p$, which refers to the maximum peak height deviation of the roughness, and $S_v$, which refers to the maximum valley depth deviation of the roughness that was evaluated over the calculated 3D surface (Figure 4d–f), were used for the calculation of the layers’ thicknesses [37]. All of the obtained values are shown in Table 2.
Figure 3. SEM images for the Ti-TiO$_2$ layers as S1 (a); S2 (b); S3 (c) and sensors Ti-TiO$_2$-CuMnO$_2$ as S1a (d); S2a (e); S3a (f).
Figure 4. 2D AFM surface images of S1 (a); S2 (b) and S3 (c); 3D AFM images for S1 (d); S2 (e) and S3 (f).
In addition, the surface roughness (measured surface area of about 1.326 pm²), which is represented by the average roughness $S_a$ and the mean square root roughness $S_q$, and the layer thickness were determined from the AFM analysis data. The topographical parameters $S_p$, which refers to the maximum peak height deviation of the roughness, and $S_v$, which refers to the maximum valley depth deviation of the roughness that was evaluated over the calculated 3D surface (Figure 4d–f), were used for the calculation of the layers’ thickness [37]. All of the obtained values are shown in Table 2.

Table 2. Surface particle sizes, nano-roughness and layer thickness.

| Sample | Etching Time (h) | Particle Size (nm) | $S_a$ (nm) | $S_q$ (nm) | $S_p$ (nm) | $S_v$ (nm) | Layer Thickness $S_p-S_v$ (nm) [38] |
|--------|-----------------|-------------------|------------|------------|------------|------------|-----------------------------------|
| S1     | 1               | 86                | 20.547     | 24.988     | 29.800     | −37.804    | 57.604                            |
| S2     | 2               | 69                | 16.560     | 20.004     | 51.492     | −56.759    | 108.251                           |
| S3     | 3               | 20                | 8.4521     | 10.758     | 104.64     | −76.487    | 181.127                           |

By evaluating the results from Figures 4 and 5 and Table 2, it was noted that the sample S3, which was etched in the HF solution (0.5 M) for 3 h, presented the smallest values for surface particle size and roughness. The data that were obtained from the AFM measurements were in accordance with those that were observed from the XRD and SEM.

Figure 5. Particle size distribution for S1 (a); S2 (b) and S3 (c).
analyses, with some differences because of the different calculation algorithms that were used. Regarding the thickness of the layers, based on the values that were obtained from the AFM measurements and the SEM images, it can be noted that the TiO$_2$ layer with the highest thickness of about 181 nm was seen in the S3 sample. The treatment times of the Ti foils in the HF solution determine the particle size as well as the thickness of the TiO$_2$ layer. Thus, the particle size is inversely proportional, and the layer thickness is directly proportional to the corrosion time.

3.2. Optical, Electrochemical and Electrical Properties

The UV-Vis absorption spectra of the synthesized Ti-TiO$_2$ layers and Ti-TiO$_2$-CuMnO$_2$ heterostructures in the range of 300–800 nm were presented in Figure 6. It was noted that the synthesized Ti-TiO$_2$-CuMnO$_2$ structures have a strong absorption in the UV range, demonstrating that the heterostructures have a strong affinity for UV light. The absorption peak of the Ti-TiO$_2$ layer was found at around 380 nm, and gradually increased with the chemical treatment time (Figure 6a). The optical band-gap energy of the as-synthesized heterostructures was determined using the Tauc plot [39] shown in Figure 6c. The $E_g$ optical band-gap energy was derived from the intersect of the straight line with the $h\nu$-axis of the Tauc plot. The estimated band gap of the Ti-TiO$_2$ is about 2.95 eV (Figure 4b), which corresponds to the rutile form of TiO$_2$ [40]. The modification of the spectra shapes shown in Figure 4b confirms the interface between TiO$_2$ and CuMnO$_2$. After the deposition of the CuMnO$_2$ thin film, the calculated $E_g$ was about 2.69 eV, 2.79 eV, and 3.07 eV depending on the chemical treatment time (Figure 6d).

![UV-Vis absorption spectra](image-url)

**Figure 6.** UV-Vis absorption spectra of the Ti-TiO$_2$ layers (a) and Ti-TiO$_2$-CuMnO$_2$ (b) heterostructures; The $a\nu$ versus $E_g$ curve for the Ti-TiO$_2$ (c) and the Ti-TiO$_2$-CuMnO$_2$ (d).
The Mott–Schottky analysis presented in Figure 7a–c shows the electronic energy levels of the Ti-TiO$_2$ (Ti support) layers and CuMnO$_2$ (FTO support) film that was investigated by electrochemical impedance measurements; conduction type and carrier concentration were calculated using the Mott–Schottky equation [26]. Figure 7a shows the positive slope for Ti-TiO$_2$ layers, suggesting the $n$-type behavior of the semiconductor, with the $V_{FB}$ values being determined as $-0.38$ V vs. NHE (S1), $-0.36$ V vs. NHE (S2) and $-0.48$ V vs. NHE (S3), with $E(\text{NHE}) = E(\text{Ag/AgCl}) + 0.197$ (unit in V). Also, the carrier densities were calculated for S1 ($1.45 \times 10^{17}$ cm$^{-3}$), S2 ($1.81 \times 10^{17}$ cm$^{-3}$) and S3 ($2.59 \times 10^{17}$ cm$^{-3}$).

For CuMnO$_2$, the Mott–Schottky plot illustrated in Figure 7b demonstrates the $p$-type characteristic with a $V_{FB}$ of about 0.98 V vs. NHE, and a calculated carrier density of about $1.74 \times 10^{18}$ cm$^{-3}$. Figure 7c shows the illustrated diagram of the corresponding conduction and valence band edges based on the band-gap energies that were calculated from UV-Vis spectra (Figure 6c,d) and the calculated $V_{FB}$ values.

![Mott-Schottky analysis of Ti-TiO$_2$ layers and CuMnO$_2$ film.](image)

**Figure 7.** Mott-Schottky analysis of (a) Ti-TiO$_2$ layers and (b) CuMnO$_2$ film; (c) diagram for corresponding conduction and valence band edges.

The current-voltage properties of the as-synthesized oxide “$n$-$p$” heterojunction, which was investigated at room temperature in dark and UV conditions, is presented in Figure 8. The $n$-TiO$_2$/$p$-CuMnO$_2$ heterojunction with a rectifying behavior was highlighted in all three cases that were investigated in the experimental program, both in dark and UV conditions. In addition, all of the cases ($I$-$V$ measurements made in the interval $-2$ and $+2$ V) showed an increased current and a reduced turn-on voltage under UV conditions.
compared to those in the dark state. This may be due to an increase in the charge-carrier concentration due to UV excitation [41].

Figure 8. Current-voltage characteristics of $n$-TiO$_2$/p-CuMnO$_2$ heterojunction for (a) S1a; (b) S2a and (c) S3a under dark, UV and Vis irradiation (Inset: ohmic contact measurements); Log from forward and reverse bias for (d) S1a; (e) S2a and (f) S3a, under dark and UV illuminated conditions.
Figure 8a–c presents the I-V measurements at different immersion times in the dark state, UV and Vis illumination. The dark state and UV light showed reduced turn-on voltages from 0.858 V to 0.513 V (for S1a), 0.980 V to 0.791 V (for S2a), and from 1.310 V to 0.812 V (for S3a). In addition, an increase in the current in the forward bias between dark and UV illumination, from 0.24 mA to 0.41 mA at S1a, from 10 mA to 13 mA at S2a, and from 0.11 mA to 0.24 mA for S3a, was noted. This can be attributed to the narrowed heterojunction interface that is generated by UV excitation [42,43]. In addition, it can be seen that the turn-on voltages increase with an increase in corrosion time, which is likely a result of the growth of the surface area. The higher specific surface area of the n-TiO2/p-CuMnO2 heterojunction can enhance light-trapping processes and increase the charge-carrier concentration in the depletion region, as well as the carrier lifetime [44,45]. The slightly higher value of the dark current in the case of the S2a sensor is possibly due to the injection of free electrons from the reverse bias. Because the ideality factor “n” is greater than 2, our junction does not block the total current on the reverse bias, thereby generating free electrons and conducting current on the forward bias [46]. The decrease in the reverse saturation current I0 (Tabel 3) for this junction supports our theory. The I-V characteristics in the visible spectrum show the variation of turn-on voltages as 0.7 V (S1a), 1.09 V (S2a), and 1.131 V (S3a) (Figure 8a–c). A small increase in the current at visible illumination in the visible spectrum show the variation of turn-on voltages as 0.7 V (S1a), 1.09 V (S2a), and 1.131 V (S3a) (Figure 8a–c). A small increase in the current at visible illumination compared to the current in the dark state, which is due to the generated photoexcitation, can also be observed. The inset of Figure 8a–c shows that the I-V characteristics for the Ti-TiO2 and CuMnO2 interface present a linear behavior, which indicates the ohmic nature of the contacts [47]. Figure 8d–f show the semi–logarithmic forward and reverse biases for the S1a, S2a, and S3a UV sensors. An increase in asymmetry between the forward and reverse biases can be noted, suggesting that all heterojunctions work at a higher rectification upon S1a, S2a, and S3a UV sensors. An increase in asymmetry between the forward and reverse biases can be noted, suggesting that all heterojunctions work at a higher rectification upon S1a, S2a, and S3a UV sensors. An increase in asymmetry between the forward and reverse biases can be noted, suggesting that all heterojunctions work at a higher rectification upon S1a, S2a, and S3a UV sensors. An increase in asymmetry between the forward and reverse biases can be noted, suggesting that all heterojunctions work at a higher rectification upon S1a, S2a, and S3a UV sensors. An increase in asymmetry between the forward and reverse biases can be noted, suggesting that all heterojunctions work at a higher rectification upon S1a, S2a, and S3a UV sensors. An increase in asymmetry between the forward and reverse biases can be noted, suggesting that all heterojunctions work at a higher rectification upon S1a, S2a, and S3a UV sensors. An increase in asymmetry between the forward and reverse biases can be noted, suggesting that all heterojunctions work at a higher rectification upon

\[ I = I_0 \left[ \exp \left( \frac{V}{nkT} \right) - 1 \right] \]

where \( I_0 \) (reverse saturation current), \( V \) (applied voltage), \( n \) (ideality factor), \( k \) (Boltzmann’s constant) and \( T \) (operation temperature). The ideality factor (n) is calculated in the dark by plotting \( \log(I)-V \), which is the slope of the straight-line region of the forward bias that is equal to \( q/nkT \) (electronic charge \( q = 1.6 \times 10^{-19} \) C, and operating temperature \( T = 298 \) K). The reverse saturation current \( (I_0) \) is found from the intercept of the straight-line region of the forward bias of the logarithmic current against the voltage, which gives us \( \log(I_0) \) [41]. These parameters are presented in Table 3.

The Sah–Noyce–Shockley formula for a classical p-n junction give an ideality factor value between 1 and 2 [49]. However, the theoretical model cannot account for the ideality

| Sample | Type | V_F (V) | I_F (A) | I_R (A) | n | I_0 (A) |
|--------|------|--------|--------|--------|---|--------|
| S1a    | Dark | 0.858  | 0.24 × 10^{-3} | 0.14 × 10^{-3} | 3.95 | 1.66 × 10^{-9} |
|        | UV   | 0.513  | 0.41 × 10^{-3} | 0.22 × 10^{-3} | -  | 1.82 × 10^{-9} |
| S2a    | Dark | 0.980  | 10 × 10^{-3}   | 3 × 10^{-3}    | 3.40 | 0.013 × 10^{-9} |
|        | UV   | 0.791  | 13 × 10^{-3}   | 4 × 10^{-3}    | -  | 0.025 × 10^{-9} |
| S3a    | Dark | 1.310  | 0.11 × 10^{-3} | 0.16 × 10^{-3} | 6.48 | 0.55 × 10^{-9} |
|        | UV   | 0.812  | 0.24 × 10^{-3} | 0.14 × 10^{-3} | -  | 3.93 × 10^{-9} |
factors greater than 2 that were found in our case [50]. Table 3 shows the obtained ideality factor that depends on corrosion time. A small difference regarding the ideality factor between the S1a and S2a sensor types, 3.95 versus 3.40, and a significant increase in the value for the sensor type S3a to an ideality factor equal to 6.48 were seen. This means that a high increase in the corrosion time can move the junction away from an ideal one. The high value of $n$ suggests that the transport mechanism of the $n$-$\text{TiO}_2/p$-$\text{CuMnO}_2$ heterojunction is not determined by the thermionic emission from the Sah–Noyce–Shockley theory, but that it results from several factors: (i) defect-assisted tunnelling; (ii) the accelerated recombination of electrons and holes in the depletion region; (iii) the existence of high-density surface states, or combinations of these mechanisms [39,51].

Figure 9 shows the photo-detective properties under UV and Vis light exposure of the heterojunction device at a bias of 2 V. The switching of the photocurrent from the “ON” to the “OFF” state could be achieved reproducibly by turning the UV illumination. The performance of the sensors was measured under UV (0.1 mW/cm$^2$) in the atmospheric environment. The response time of the heterojunction sensor upon UV lighting depends on the corrosion time, and it was about 6.29 s (S1a), 1.56 s (S2a) and 0.58 s (S3a), but only S1a required a recovery time of about 4.89 s. This improvement of the response and recovery speed that depend on the parameters of the production process resulted from the increase in surface area favoring light trapping.

![Figure 9. UV and Vis time-dependent photo-detective properties of the sensors at light exposure (ON/OFF = 20 s).](image)

The photocurrent measurement in the dark was about 0.057 mA (S1a), 2.52 mA (S2a), and 0.095 mA (S3a), and under UV illumination for 20 s, the current increases to 0.262 mA (S1a), 12.58 mA (S2a), and 0.22 mA (S3a). The sensitivity of the sensor was calculated as a ratio between photocurrent to darkness ($I_{\text{UV}}/I_{\text{DARK}}$), which was about 4.89 for S1a, 4.99 for S2a, 2.31 for S3a. The responsivity values were calculated using Equation (2) [48]:

$$ R = \frac{I_{\text{UV}} - I_{\text{DARK}}}{P_{\text{opt}} \cdot S} $$

where $I_{\text{UV}}$ is the photocurrent at UV lighting, $I_{\text{DARK}}$ is the current in the dark, $S$ is the effective area (1 cm$^2$) and $P_{\text{opt}}$ is the optical power of the UV source. From this equation, knowing that the light power is 0.1 mW/cm$^2$, the responsivity values of the as-prepared $n$-$\text{TiO}_2/p$-$\text{CuMnO}_2$ heterojunction sensors are 2.05 A W$^{-1}$ cm$^2$ (S1a), 100.6 A W$^{-1}$ cm$^2$ (S2a) and 1.25 A W$^{-1}$ cm$^2$ (S3a).

The rejection ratio between UV and visible light was calculated by the division of the maximum responsivity in the UV range to the responsivity at visible light [52]. Therefore, the UV rejection ratio $R_{\text{UV}}/R_{\text{vis}}$ of the heterojunction photodetector was about 41 (S1a), 91.45 (S2a) and 41.66 (S3a), indicating that the $n$-$\text{TiO}_2/p$-$\text{CuMnO}_2$ heterojunction could
work properly as a solar-blind UV sensor. The responsivity at visible light was calculated based on Equation (2) by replacing $I_{\text{vis}}$ with $I_{\text{uv}}$ (the photocurrent at visible light), due to the fact that visible light power is 0.2 mW/cm$^2$, and the resulting values were about 0.05 A W$^{-1}$ cm$^2$ (S1a), 1.1 A W$^{-1}$ cm$^2$ (S2a) and 0.03 A W$^{-1}$ cm$^2$ (S3a). The increases in the response and recovery speed for S2a and S3a is probably due to the pair of electron–hole in the recombination center. Thus, the increase in the velocity saturation during UV illumination determines the decrease in the resistance to the freely flowing UV-generated electrons in the channel [53]. In addition, the increase in the carrier densities for S2 and S3 that were highlighted in the Mott–Schottky analysis, which led to the increase in the recombination speed for the junction, further explains the increases in response and recovery speed. From the comparison of the physical parameters of the junctions, it can be seen that there is a close correlation between the ideality factor ($n$) and the sensitivity of the UV photodetector. Additionally, the sensitivity of S3a decreases almost proportionally to the difference in the S2a ideality factor. This means that approaching an ideal junction can lead to an improvement in sensitivity [54]. The best performance of the S2a sensor (sensitivity, responsivity, response and recovery speed) compared to S1a and S3a, was demonstrated by several parameters: crystallite size, porosity, layer thickness, band-gap energy values and flat-band potential. The thickness of the layer is a parameter that has a direct effect on the optical band gap. From the UV-Vis optical measurements (see Figure 6) it was observed that the optical band-gap energy of the Ti-TiO$_2$-CuMnO$_2$ heterostructures (see Figure 6b,c,d) decreases proportionally with the thickness of the layer. The increase in the thickness of the TiO$_2$ layers determines the addition of new energy levels, thereby creating new “cross-bridges” from the electrons that are transmitted between the valence band and conduction band, which increases the electron lifetime and decreases the recombination rate of the electrons [55]. In addition, the roughness can improve the response and recovery speeds because of the increasing of the contact surface between TiO$_2$ and CuMnO$_2$, leading to the generation of more pairs of electron-holes. Furthermore, the enhanced sensitivity and responsivity of the S2a sensor may be due to both the increased specific area [56] and the balance that was achieved between the size of the crystallites and charge-carrier concentration in the heterojunction interface [57,58].

4. Conclusions

UV photodetectors based on $n$-TiO$_2$ and $p$-CuMnO$_2$ heterojunction were successfully obtained via a simple, reproducible and inexpensive method following two steps. Firstly, the TiO$_2$ layers were grown on Ti foil by thermal oxidation (Ti-TiO$_2$), afterwards the CuMnO$_2$ films were deposited onto the surface of the TiO$_2$ layers by the Doctor Blade method. The structural characteristics of the Ti-TiO$_2$ layers and Ti-TiO$_2$-CuMnO$_2$ sensors were investigated by XRD technique, which confirmed the phases’ stability and purity of the as-synthesized materials. Morphological characteristics that were determined by SEM and AFM underlined that the TiO$_2$ layers were grown and oriented in clearly defined and delimited directions by the curved surfaces of the polyhedral structure. The CuMnO$_2$ films uniformly covered, without cracks, the surface of the TiO$_2$ layers following their polyhedral shape. From the AFM analysis, it was observed that the treatment times of Ti foils in HF solution influences the particle size and thickness of the TiO$_2$ layer. As the corrosion time increases, the particle size decreases, and the layer thickness increases. The thickness and the roughness of the TiO$_2$ layer directly influence the opto-electrical characteristics of the sensors. From the Mott–Schottky measurements, it was observed that the flat-band potential $V_{FB}$ and the carrier densities (linear increase) for TiO$_2$ are influenced by the layer thickness. It was also observed that there is a correlation between the evolution of the flat band and the sensitivity of the sensors, which is better represented by S1a and S2a than S3a.

The electrical parameters of the $n$-TiO$_2$/$p$-CuMnO$_2$ heterojunction in the dark and UV illumination conditions highlighted that the minimum voltage of the junction, which is the voltage necessary for starting the conduction of current in the forward direction (turn-on voltage), increases according to structure of the Ti-TiO$_2$ layers. Thus, sensor S3a had the
highest voltage values, which in the dark state was about 1.310 V, and in UV conditions was about 0.812 V. Also, a close correlation between the ideality factor and the sensibility in UV illumination have been established. The sensor S2a displays a sensibility value of 4.99, a responsivity of 100.6 mA mW⁻¹ cm², and a high-speed response time of about 1.56 s. A decrease in the grain size (to approx. 25 nm) leads to a decrease in the structural stability of the junction and has an undesirable effect on the temporal stability of the sensor. The UV-Vis rejection ratios were determined by illumination in the Vis spectrum, and the obtained results show that the sensor acts as a suitable selective UV photodetector. In conclusion, the method of thermal oxidation that was used for obtaining the “n” component (Ti-TiO₂) of the heterojunction provides a simple choice for the achievement of oxide layers with suitable structures for the development of UV sensors (Ti-TiO₂-CuMnO₂). The results show that the UV photodetectors that are based on the n-TiO₂/p-CuMnO₂ heterojunction and obtained through a new approach have great potential applications in light detection systems.

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