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Paulina Sawicka-Chudy, Maciej Sibiński, Elżbieta Rybak-Wilusz, Marian Cholewa, Grzegorz Wisz, and Rostyslav Yavorskyi

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Paulina Sawicka-Chudy,[1,a)] Maciej Sibiński,[2] Elżbieta Rybak-Wilusz,[3] Marian Cholewa,[1] Grzegorz Wisz,[1] and Rostyslav Yavorskyi[4]

AFFILIATIONS

[1]Institute of Physics, College of Natural Science, University of Rzeszow, 1 Pigonia Street, 35-317 Rzeszow, Poland
[2]Department of Semiconductor and Optoelectronics Devices, Lodz University of Technology, Wólczańska 211/215, 90-924 Lodz, Poland
[3]Department of Heat Engineering and Air Conditioning, Faculty of Civil and Environmental Engineering and Architecture, Rzeszow University of Technology, 12 Powstańców Warszawy Street, 35-959 Rzeszow, Poland
[4]Vasyl Stefanyk Precarpathian National University, T. Shevchenko, 57, 76-018 Iwano Frankiwsk, Ukraine

[a)]**Author to whom correspondence should be addressed:** psawicka@ur.edu.pl

ABSTRACT

Copper oxide-titanium dioxide (TiO_2) p–n junctions are promising materials for photovoltaic devices and may reduce production costs due to their low cost and inexpensive production methods compared with silicon solar cells. The present review compares solar cells made with copper oxides combined with TiO_2–TiO_2/Cu_2O and TiO_2/CuO heterojunctions, and "cascade heterojunction systems." First, we describe the main properties of titanium (IV) dioxide (TiO_2), cuprous oxide (Cu_2O), and cupric oxide (CuO), and their potential applications. Next, we explain the concept of copper oxide and TiO_2 heterojunctions. We summarize and present the photovoltaic characteristics (efficiency, fill factor, circuit current density, and open circuit voltage), thickness, preparation method, and electrode type for solar cells comprising copper oxide and TiO_2. The efficiency of the solar cells ranged from 0.0005% to 1.62%. The thickness of the TiO_2 and cupric oxide layers ranged from 0.06 to 16 μm, and from 0.18 to 1.5 μm, respectively, depending on the fabrication method. Additionally, we review and discuss the available combinations of copper oxide with other materials (Cu_2O with ZnO, CuO with ZnO, and CuO with Si), as well as the effect of the thickness of the copper (I) oxide and copper (II) oxide on the solar cell performance. Finally, we present aspects to improve the conversion efficiency of heterojunction solar cells with copper oxides combined with TiO_2. This review will be useful for the construction and further development of thin-film solar cells.

I. INTRODUCTION

Solar cells are becoming increasingly important in light of foreseeable increases in energy use and limitations of natural fossil fuel resources.[1] Solar cells were invented in the 19th century, but the first practical photovoltaic (PV) solar cells were developed in 1954, producing a conversion efficiency of ~6%.[2,3] In 1947, Telkes achieved an efficiency of ~1% using thermoelectric junctions.[2,4] In 1958, silicon solar cells were first applied to the satellite Vanguard 1,[5] and in 1976, Carlson and Wronski[6] fabricated α-Si:H solar cells at the RCA Laboratory with an energy conversion efficiency of 2.4%. Green[7] recently reported an energy conversion efficiency of 26.7% achieved on Si (crystalline cell) with an area of 79 cm^2. The manufacture of silicon solar cells, however, requires expensive materials and production processes. Metal oxide (MO) semiconductor(s) have several advantages for PV devices, including nontoxicity, abundance, chemical stability allowing for the material to be deposited under ambient conditions,[8,9] simple structure, simple fabrication process, low temperature processing, photosensitivity, and potentially lower cost due to the availability of inexpensive materials and production methods.[9–12] Although MO semiconductors have much lower efficiencies,[3,13–20] they have become a recent focus of fundamental research.[21–25]

Copper oxides combined with TiO_2 are promising materials for optoelectronics, which are potentially useful for inexpensive and competitive solar cell construction.[26] Copper is a cheap material,

e.g., gold is 6000 times more expensive.[27] Furthermore, Cu_2O/TiO_2 heterostructures have the ability to store multiple electrons in thin film(s);[28] the theoretical limit of efficiency of a defect-free TiO_2/CuO solar cell is ~20%,[29–31] ~16% with a CuO film thickness of only 1.5 μm, and 28.6% for a tandem structure of $TiO_2/CuO/Cu_2O$.[3] Metal oxide solar cells, however, may have a large number of defects at the heterojunction interface and are not able to achieve both *n*-type and *p*-type controllable conductivity.[3]

In our review, we present the state of the art as well as our technological experience with solar cells made with copper oxides combined with TiO_2 and compare their PV characteristics. We have been fabricating TiO_2/Cu_2O and TiO_2/CuO thin-film heterojunction solar cells using direct current (DC) magnetron sputtering,[29,32] and describe copper and TiO_2-based solar cells. This review should be useful for the construction and further development of thin-film solar cells.

II. PROPERTIES AND APPLICATIONS OF TITANIUM DIOXIDE AND COPPER OXIDES

A. Properties of titanium dioxide

Understanding the material properties of TiO_2 and copper oxides will help to clarify the mechanisms of heterojunction solar cells based on these metal oxides.

Titanium dioxide was discovered in 1795[33] and has been studied since 1972.[34] It is a key semiconductor used for the development of photocatalysis[35] and solar cells. TiO_2 is usually used in dye-sensitized solar cells. In a dye, TiO_2 captures photons of visible light radiation at a lower energy than its band gap and tunnels the electrons produced by the light harvester to external contacts.[22] Anatase and rutile (tetragonals), and brookite (orthorhombic) are crystalline polymorphs of TiO_2.[36,37] Rutile is thermodynamically more stable than brookite and anatase. Heating brookite and anatase at a temperature of ~900 °C converts them to rutile.[29] Brookite is the least stable of the three polymorphs.[38] When the substrate temperature is low during deposition, amorphous TiO_2 is observed.[38,39] Table I shows details of the parameters of TiO_2.

TiO_2 can function as an indirect gap semiconductor.[47] The band gap energy of anatase and rutile is greater than 3 eV.[54,55] Titanium dioxide absorbs a small fraction of the spectral solar irradiance.[56] At wavelengths shorter than 387 nm (anatase) and 413 nm (rutile), electron–hole pairs are formed by the solar spectrum.[38,56,57] Titanium dioxide absorbs less than 5% of the solar spectrum and is thus used to reduce the band gap for better absorption of the solar spectrum or as a transparent window-layer.[3,58] In TiO_2, electrons and holes not consumed upon generation will rapidly undergo recombination [$(3.2 \pm 1.4) \times 10^{-11}$ cm^3/s].[59] TiO_2 is highly stable against mechanical abrasion, chemical attacks, and high temperatures.[30] TiO_2 has potential applications for solar energy

TABLE I. Parameters of TiO_2.

Parameter	Anatase	Rutile	Brookite	References
Phase	Tetragonal a = 3.785 Å, c = 9.514 Å	Tetragonal a = b = 4.593 Å, c = 2.959 Å	Orthorhombic a = 5.456 Å, b = 9.182 Å, c = 5.143 Å	40
Film density (g/cm^3)	3.84	4.25	4.11	31 and 41–43
Refractive index at 550 nm (reference value)	2.57	2.70	[a]	44 and 45
Resistivity (Ω cm)		$\sim 10^{13}$		46
Band gap energy (eV)	3.20	3.0, 3.05	2.96	45 and 47
Electron affinity (eV)		3.9, ~4.1, 4.2		48–50
Absorption coefficient for ultraviolet photons (1/cm)		$\sim 10^5$–10^6		51–53
Dielectric permittivity (relative)		10		30
CB (conduction band) effective density of states ($1/cm^3$)		2×10^{17}		
VB (valence band) effective density of states ($1/cm^3$)		6×10^{17}		
Electron mobility (cm^2/Vs)		100		
Hole mobility (cm^2/Vs)		25		
Shallow uniform donor density ($1/cm^3$)		10^{17}		
Shallow uniform acceptor density ($1/cm^3$)		0		
Band to band recombination rate ($cm^3\ s^{-1}$)		1.3×10^{-9}		
Valence band edge (eV)		−7.1		43
Conduction band edge (eV)		−3.9		

[a]No data.

conversion, solar cells (especially as the active component in dye-sensitized solar cells, optical sensors, quantum dots, and optical waveguides), photocatalysis, catalysis, environmental purification and separation, water treatment, antibacterial materials, multilayer mirrors, antireflection coatings, dielectric interference filters, and gas-sensing agents, and TiO_2 can be used in artificial heart valves due to its high blood compatibility.[39,54,60–63] TiO_2 films are also used as buffer layers inserted between copper oxides and transparent conductive oxides, indium tin oxide, and fluorine-doped tin oxide (FTO) layers to mitigate nonideal heterojunctions.[64,65] Buffer layers improve band-alignment across the heterojunction and reduce the interface defect density and interfacial recombination.[64]

TiO_2 thin films are obtained by various techniques: metallo-organic sol-gels,[66] atomic layer deposition,[67] electrophoretic immobilization of TiO_2 powder,[68] pulsed-laser deposition,[69–75] reactive radio frequency sputtering,[76–81] mixing of commercially available nanopowders,[82] reactive DC sputtering,[83–86] chemical vapor deposition,[87,88] ion beam sputtering-cold condensation,[89] and plasma-enhanced chemical vapor deposition.[90]

B. Properties of cuprous oxide (Cu_2O) and cupric oxide (CuO)

Copper oxides are available in three forms: Cu (I) oxide (Cu_2O, cuprous oxide), Cu (II) oxide (CuO, cupric oxide), and Cu_4O_3.[43,91] Cu_2O was discovered before germanium and silicon.[92] Cu_2O and CuO semiconductors exhibit many interesting characteristics that are useful for solar cells,[93] with potential applications for solid state gas sensor heterocontacts, heterogeneous catalysts, and microwave dielectric materials.[94–100] Semiconductors are also promising materials for photocatalytic[101] hydrogen production, especially Cu_2O.[91,102–105] The potential of Cu_2O for use in solar cells was first recognized in 1920.[92,105] Table II shows the detailed parameters of copper oxides.

Copper oxides are *p*-type semiconductors[118] with band gaps ranging from 1.0 to 2.1 eV for CuO[113,119–121] and from 2.0 to 2.6 eV for Cu_2O.[119,107] CuO has a smaller band gap than Cu_2O and therefore absorbs more photons. Copper oxides are low cost and nontoxic, exhibit good electron mobility, but have a fairly high minority carrier diffusion length[60] as well as poor or inadequate photostability. Additionally, copper (I) oxides possess higher photocatalytic activity than copper (II) oxides for degrading organic compounds.[91,105,106] Copper oxide films can be obtained by many techniques. Table III shows some properties (band gap type, gap, crystallite size, and nanocrystal shape) of copper oxide samples prepared by different production methods.

The parameters of copper oxides can be controlled. The optical band gap and crystallite size depend on the preparation method. For example, as the thickness of the structure increases, the band gap energy decreases from 2.48 eV to 2.31 eV,[122] and the grain size increases from 31 nm to 42 nm with an increase in oxygen pressure.[125] Decreasing the nanocrystal size leads to an increase in the internal surface and interface areas (for equal CuO concentration in

TABLE II. Parameters of the common copper oxides.

Parameter	Cu_2O	References	CuO	References
Phase	Cubic, a = 4.27 Å	40	Monoclinic, a = 4.6837 Å, b = 3.4226 Å, c = 5.1288 Å	40
Band gap energy (eV)	2.0–2.6	106	1.0, 1.2, 2.1	20, 60, 113, and 114
Electron affinity (eV)	3.20	103 and 104	4.07, 3.23, 3.80	3 and 115
Dielectric permittivity (relative)	7.11	103 and 95	18.10	3
CB (conduction band) effective density of states ($1/cm^3$)	2.02×10^{17}	103 and 108	3.0×10^{19}	3
VB (valence band) effective density of states ($1/cm^3$)	1.1×10^{19}	103 and 108	5.5×10^{20}	3
Conduction valence bands (eV)	[a]	[a]	−4.27 to −2.70	82
Valence band edge (eV)	−4.32 to −4.0	101	−5.34 to −4.80	43, 82, and 115
Electron mobility (cm^2/Vs)	200	103 and 108	0.1	3
Hole mobility (cm^2/Vs)	80	103 and 95	10.0	3
Hole effective mass	$0.69m_0$	109	$0.54m_0$–$3.72m_0$	43 and 116
Electron effective mass	$0.99m_0$	109	$0.14m_0$–$0.17m_0$ $0.16m_0$–$0.46m_0$	43 and 117
Shallow uniform donor density (cm^{-3})	0	3	0	3
Shallow uniform acceptor density (cm^{-3})	1×10^{18}	103 and 30	1×10^{16}	3
Conductivity $(\Omega\ cm)^{-1}$	10^{-6} to 10^{-8}	110	1.05×10^{-2}, 6.3×10^{-2}	43
Hole concentration (cm^{-3})	10^{16}	111	6.69×10^{16} cm^{-3}, 4.0×10^{18} cm^{-3}	43
Hall mobility ($V\ cm^{-1}\ s^{-1}$)	30, 100, 53	111 and 112	0.98, 0.1	43 and 109

[a]No data.

TABLE III. Properties of copper oxide films prepared by different methods.

Preparation method	Optical band gap (eV)	Crystallite size (nm)	Reference
Pyrolysis technique	[a]	20–170	95
SILAR method	2.31–2.48	7.0–8.0	122
Thermal evaporation	1.50–1.85	27–39	123
Chemical vapor deposition	[a]	500	124
Pulsed laser deposition	2.52, 2.42, 2.12	31–42	125
Sol–gel	2.1, 1.9	[a]	126
Magnetron sputtering	1.58	120, 220	29

[a]No data.

TiO_2) and results in interfacial defects and increasing recombination losses.[127]

III. THE SHARED CONCEPT BETWEEN COPPER OXIDES AND TIO_2 HETEROJUNCTIONS

A solar cell with combined *p*-type and *n*-type semiconductors is called a blended or bulk-heterojunction solar cell.[128] TiO_2/CuO or TiO_2/Cu_2O structures are attractive candidates for photocatalytic applications[129] and PV solar cells. To obtain good efficiency when combining the two semiconductors, it is necessary to obtain high efficiency for each of the individual semiconductors, which are more negative than those of large-gap semiconductor(s).[130,131] The conduction band edges of Cu_2O and CuO are −1.64 and 0.96 V,[132,133] respectively. CuO/TiO_2 composites have been tested in processes such as hydrogen production,[134–139] CO_2 reduction,[139–142] pollutant degradation,[139,142,143] and microorganism inactivation.[139,144,145]

To create heterojunction systems, both semiconductors must possess different energy levels from their corresponding valence and conduction bands,[146] which improves charge carrier separation and increases the lifetime of the charge.[147,148] The valence (Ev) and conduction (Ec) bands of TiO_2 are lower than those of Cu_2O and CuO.[149] Figure 1 shows the energy level band diagrams of the Cu_2O/TiO_2 and CuO/TiO_2 thin-film heterojunction solar cells.

Conduction band discontinuity (ΔEc) can be calculated using the following equation:[47,150]

$$\Delta Ec = \sigma_n + \sigma_p - E_{gCu_2O,CuO} + q \cdot V_D, \quad (1)$$

where σ_n is the activation energy of TiO_2 σ_n = 0.72 eV, σ_p is the position of the Fermi-level for Cu_2O or CuO above the valence band, $\sigma_p = k \cdot T \ln(N_V/N_A)$, kT = 0.026 eV, N_V is the effective state density in the valence band $N_v = 1.9 \times 10^{19}$ 1/cm^3[47] for *p*-Cu_2O, and $N_v = 5.5 \times 10^{20}$[3] for *p*-CuO, N_A is the acceptor concentration $N_A = 3.5 \times 10^{18}$ 1/cm^3[47] for *p*-Cu_2O, and $N_A = 1 \times 10^{16}$ 1/cm^3.[3] V_D is the total diffusion potential, q is the electronic charge 1.6×10^{-19} C, qV_D = 0.98,[47] and E_g is the energy band gap (Cu_2O, E_g = 3.08 eV[47,151] and CuO, E_g = 1.2 eV).[20] The experimental value of ΔEc for Cu_2O is 0.48 eV, and the theoretical value for Cu_2O is 0.6 eV[47] and for CuO, 0.68 eV.

Valence band discontinuity (ΔEv) is calculated according to the following relation:[47]

$$\Delta Ev = E_{gTiO_2} - E_{gCu_2O,CuO} - \Delta Ec, \quad (2)$$

where ΔEv is 1.37 eV for Cu_2O/TiO_2 and 1.32 eV for CuO/TiO_2.

IV. COPPER OXIDE–TITANIUM DIOXIDE STRUCTURES: STATE OF THE ART

In 1999, Song *et al.*[152] first produced different types of copper with TiO_2. Although they considered that copper would improve the photocatalytic activity of TiO_2, they found that using the oxidized form of copper on TiO_2 actually decreased the photocatalytic efficiency.[152] Many researchers have manufactured TiO_2 and copper oxide thin films and studied their photocatalytic efficiency.[141,153–168] In our review, we paid special attention to TiO_2 and copper oxide heterojunctions for PV devices.

Rokhmat *et al.*[169] developed $Cu(NO_3)_2{\cdot}3H_2O$-containing TiO_2 by combined electroplating and spraying methods. PV devices were fabricated by forming cells using polymer electrolyte and aluminum counter electrodes. Additionally, the PV devices were immersed in 0.125M NaOH for 10 min. Next, they illuminated the PV devices with a 500 W halogen lamp for 15 min. Finally, they dried the PV devices at room temperature. Current-voltage (I-V) curves of the PV devices were measured at 120 W/m^2. The authors prepared solar cells with amounts of $Cu(NO_3)_2{\cdot}3H_2O$ ranging from 0% to 2 wt. %. The circuit current, open circuit voltage, fill factor (FF), and efficiency were in the range of 0.07–0.068 mA, 0.135–0.5 V,

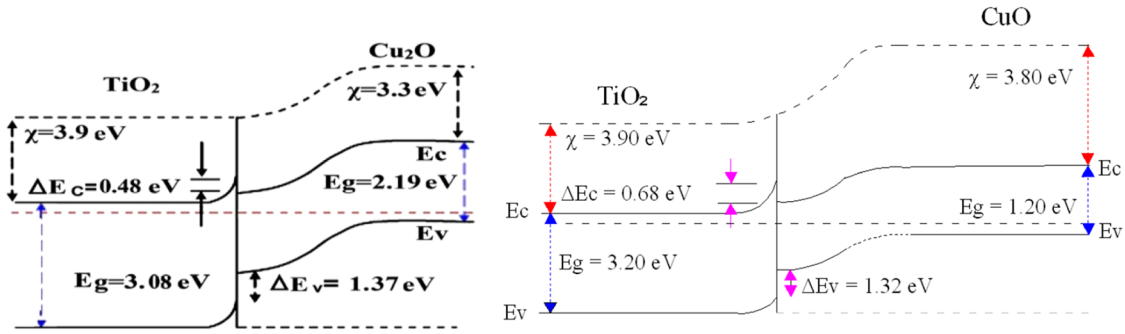

FIG. 1. Energy level band diagram of Cu_2O/TiO_2 (left), based on Ref. 47. Copyright 2019 Elsevier. Reprinted with permission from Hussain *et al.*, Thin Solid Films **522**, 430–434 (2012). Copyright 2012 Elsevier. CuO/TiO_2 thin-film heterojunction solar cells (right). Eg, energy band gap; χ, electron affinity; own current study based on Ref. 47.

0.12%–0.24%, and 0.0017%–0.04%, respectively. The highest efficiency was achieved at 1.4 wt. % $Cu(NO_3)_2{\cdot}3H_2O$. Additionally, to increase the performance of the PV devices, copper particles were placed between the TiO_2 particles by electroplating, and then the electrolyte was treated with NaOH. The efficiency of these solar cells after electroplating was 0.35%, and it increased to 1.24% after treatment with NaOH.[169]

In 2002, Siripala *et al.*[170] prepared Cu_2O/TiO_2 heterojunction structures by electrochemical deposition of Cu_2O on Ti foil. A photoresponse demonstrating efficient light-induced charge carrier separation in TiO_2–copper (I) oxide system(s) was observed. The electrode was illuminated using a Xe lamp spliced at a frequency of 700 W/m^2. Figure 2 shows photoresponses of the Cu_2O/TiO_2 with a RuO_2 counter electrode and Fig. 3 with a Pt counter electrode. The area of the counter electrodes was 2 cm^2. The authors concluded that the use of the RuO_2 counter electrodes meaningfully increased the photocurrent. Additionally, they suggested that the TiO_2 films successfully protected the copper (I) oxide layer against photocorrosion without decreasing the efficiency.[162]

Zainun *et al.*[128] prepared Cu_2O/TiO_2 thin films by squeegee and electrochemical deposition methods. They then fabricated metal electrodes (evaporating indium) on the film to form cells. Figure 4 shows the scheme for the Cu_2O/TiO_2 with the electrodes. The authors characterized the optical and structural properties of the films and measured the photoresponse of the cell. I–V characterization was measured for air mass (AM) 1.5 at 100 mW/cm^2 and for three samples with various Cu_2O deposition times (5, 10, and 15 min). The authors reported PV characteristics of cells only for the 10-min deposition, which had an efficiency of 0.0005%.[128] Figure 5 shows the J–V curves for Cu_2O/TiO_2 with various Cu_2O deposition times.

The use of nanotube arrays in Cu_2O/TiO_2 heterojunctions is widely studied.[171,172] Hou *et al.*[172] prepared Cu_2O/TiO_2 nanotube p–n junction arrays using a photoreduction method, but there was no PV effect[172] Li *et al.*[171] created 10 Cu_2O/TiO_2 p–n heterojunctions by combining two methods. TiO_2 nanotube arrays were prepared using a two-step anodization process and then *p*-type Cu_2O was electrodeposited into the TiO_2 nanotube channels. The solar cells were annealed at 200 °C in flowing Ar (200 SCCM) for 1 h to make the Cu_2O thin film more continuous and uniform. Next, the top contact electrode was prepared with a gold film

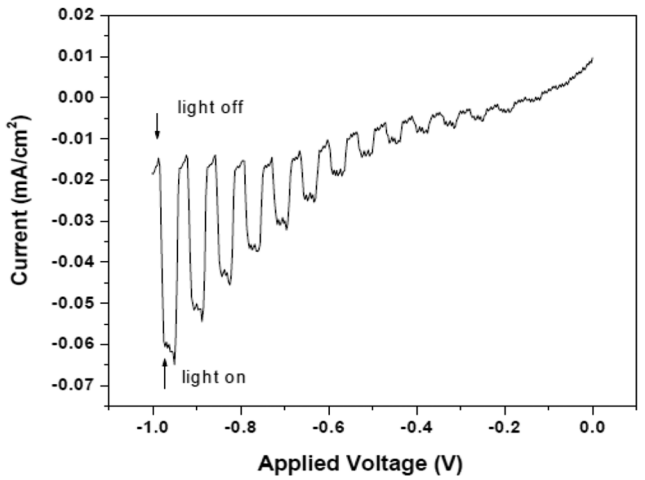

FIG. 2. The Cu_2O/TiO_2 electrode photocurrent with RuO_2 counter electrode. Reprinted with permission from Siripala *et al.*, Sol. Energy Mater. Sol. Cells **77**, 229–237 (2003). Copyright 2003 Elsevier.

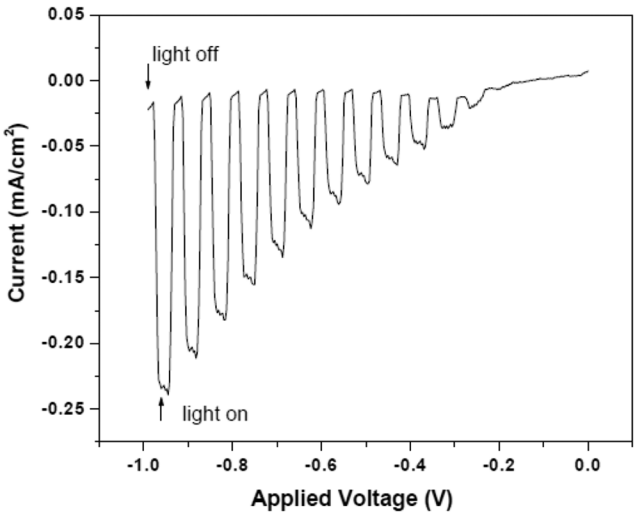

FIG. 3. The Cu_2O/TiO_2 electrode photocurrent with Pt counter electrode. Reprinted with permission from Siripala *et al.*, Sol. Energy Mater. Sol. Cells **77**, 229–237 (2003). Copyright 2003 Elsevier.

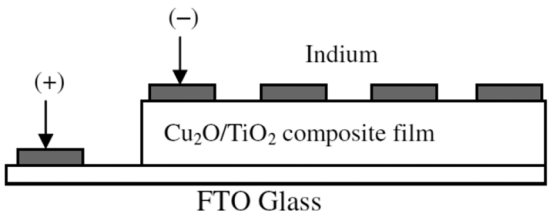

FIG. 4. Scheme for Cu_2O/TiO_2 with electrodes. Reprinted with permission from Zainun *et al.*, Mater. Lett. **66**, 254–256 (2012). Copyright 2012 Elsevier.

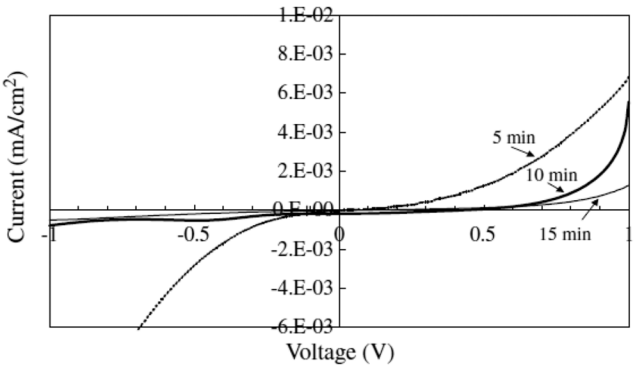

FIG. 5. J–V curves for Cu_2O/TiO_2 with different Cu_2O deposition times. Reprinted with permission from Zainun *et al.*, Mater. Lett. **66**, 254–256 (2012). Copyright 2012 Elsevier.

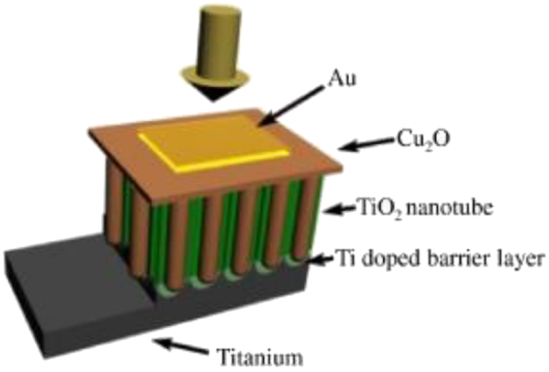

FIG. 6. Schematic diagram of Cu_2O/TiO_2. Reprinted with permission from Li *et al.*, Chem. Phys. Lett. **501**, 446–450 (2011). Copyright 2011 Elsevier.

(10-nm thick) by coating onto the Cu_2O film. The I-V curves of the solar cells were measured at 100 mW/cm^2 under simulated air mass (AM) 1.5 illumination. The open circuit voltage (V_{oc}), short circuit current density (J_{SC}), and fill factor (FF) of the Cu_2O/TiO_2 solar cells were 0.09–0.25 V, 0.1–0.33 mA/cm^2, and ~0.27, respectively. Additionally, annealing the solar cells improved the PV parameters. The efficiency was ~0.01%, V_{oc} = 0.1 V, J_{SC} = 0.33 mA/cm^2, and FF = 0.27.[171] Figure 6 shows a schematic of Cu_2O/TiO_2, and Fig. 7 shows the J–V characteristics before (left) and after annealing (right).

Pavan *et al.*[9] produced TiO_2/Cu_2O solar cells by spray pyrolysis. The authors generated PV devices with varying TiO_2 and Cu_2O layer thicknesses and the films were fabricated to form cells used on silver as a back contact. The front electrode was made of FTO. Additionally, a metal frame was soldered to the solar cell. Pavan *et al.*[9] studied the impact of layer thicknesses on the PV device performance. The thickness of TiO_2 ranged from 0.6 to 0.32 μm and that of Cu_2O ranged from 0.18 to 0.58 μm. They observed the best results when the thickness of the Cu_2O film was greater than 500 nm: V_{oc} up to 350 mV and J_{SC} of 0.4 mA/cm^2. Figure 8 shows a cross-section view of the solar cell, and Fig. 9 shows dark and light J-V measured at the top of the solar cell. Pavan *et al.*[9] concluded that to improve the PV characteristics of TiO_2/Cu_2O, the conduction band offset at the n-TiO_2/p-Cu_2O interface had to be reduced and larger higher-quality Cu_2O grains had to be synthesized.

Rokhmat *et al.*[60] also reported the construction of TiO_2/CuO and TiO_2/CuO/Cu solar cells. The TiO_2/CuO/Cu solar cells were created using a fixed current electroplating and spray method with varying electroplating currents (0.1–100 mA) for 10 s. The PV devices were fabricated by cells formed using polymer electrolyte and aluminum counter electrode(s). The I-V characteristics were measured at an intensity of 120 W/m^2. First, the authors compared solar cells before and after adding the copper particles with a current source of 1.0 mA for 10 s. Circuit-current, open circuit voltage, FF, and efficiency were 0.8 mA, 0.62 V, 0.33%, and 0.14%, respectively, for TiO_2/CuO, and 0.12 mA, 0.61 V, 0.35%, and 0.21%, respectively, for TiO_2/CuO/Cu. Next, the authors changed the electroplating current and found that the efficiency was best (0.80%) at 10 mA. Finally, the I-V characteristics of TiO_2/CuO/Cu were measured at various electroplating times with a constant electroplating current of 10 mA. Circuit-current, open circuit voltage, FF, and efficiency were in the range of 0.05–0.72 mA, 0.58–0.6 4 V, 0.34–0.42, and 0.16%–1.62%, respectively. The best result was achieved when the electroplating process was 20 s long.[60]

Hussain *et al.*[47] fabricated Cu_2O/TiO_2 by electrodeposition of Cu_2O structure on a radiofrequency sputtered TiO_2 film. The counter electrode was platinum foil and the reference electrode was Ag/AgCl (4M KCl). Finally, an indium contact was stuck to the Cu_2O thin layer. The authors characterized the solar cell by scanning electron microscopy, X-ray diffraction (XRD), and UV spectroscopy. Furthermore, they performed I-V and C–V measurements. The light intensity was set at 90 mW/cm^2. The maximum FF, power conversion efficiency, short circuit current density, and open circuit voltage was ~0.36, ~0.15%, 0.0027 A/cm^2, and 0.34 V, respectively. They concluded that the low efficiency may have been due to "band discontinuity at the interface edges," "fast electron hole pair recombination," "defects at the interface," "a large lattice mismatch," or "the exits of other planes of Cu_2O".[47] Figure 10 shows the I-V curves of the Cu_2O/TiO_2.

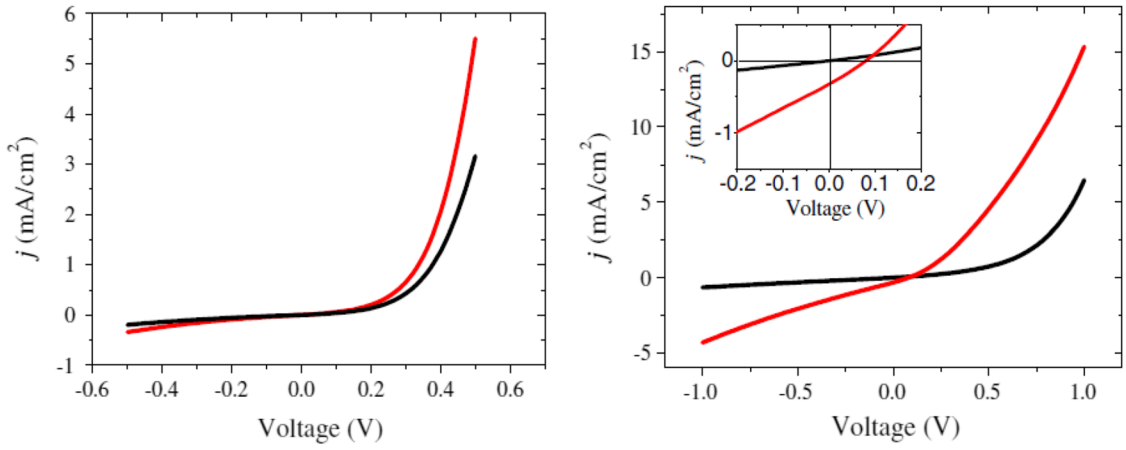

FIG. 7. J–V curves before (left) and after annealing (right). Reprinted with permission from Li *et al.*, Chem. Phys. Lett. **501**, 446–450 (2011). Copyright 2011 Elsevier.

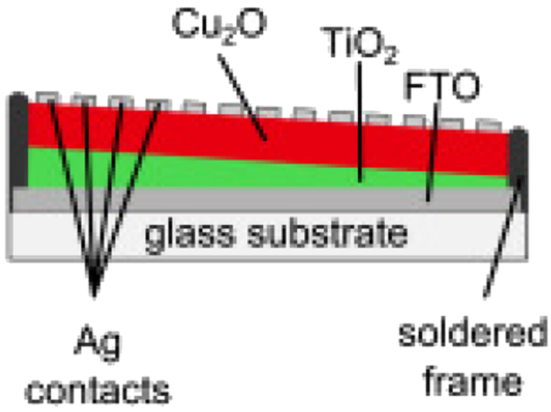

FIG. 8. Cross-section view of TiO_2/Cu_2O. Reprinted with permission from Pavan *et al.*, Sol. Energy Mater. Sol. Cells **132**, 549–556 (2015). Copyright 2015 Elsevier.

Hussain *et al.*[114] also reported on Cu_2O/TiO_2 thin-film heterojunctions in which the TiO_2 films were created via anodization of Ti foil, and the Cu_2O films were deposited on the TiO_2 film by electrodeposition. In this experiment, the authors studied the structural and morphological properties, performed X-ray diffraction (XRD) analysis, and measured the C–V and I–V characteristics. The turn on voltage of the device was 520 mV. On the basis of a C–V graph, the authors estimated that the effective carrier concentration was $N = 8 \times 10^{22}$ $1/m^3$ and the built-in potential was ~0.80 V.[114] Figure 11 shows the C^{-2}–V characteristics of this Cu_2O/TiO_2 PV device.

Ichimura and Kato[106] described TiO_2/Cu_2O solar cells prepared using two chemical techniques. The TiO_2 structures were manufactured by electrophoretic deposition using a TiO_2 sol solution on an indium-tin-oxide glass substrate. The Cu_2O thin films

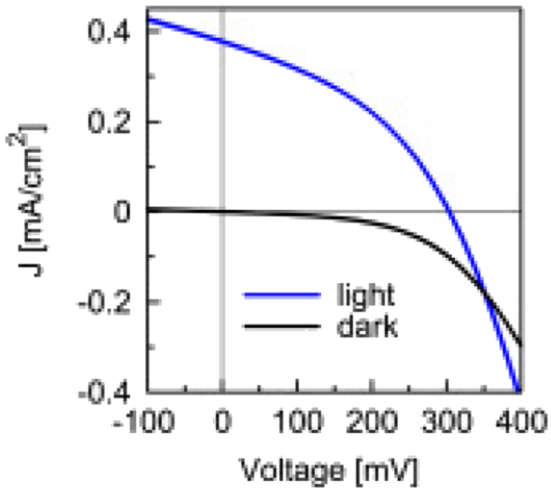

FIG. 9. Light and dark and J-V measured at the top of the solar cell. Reprinted with permission from Pavan *et al.*, Sol. Energy Mater. Sol. Cells **132**, 549–556 (2015). Copyright 2015 Elsevier.

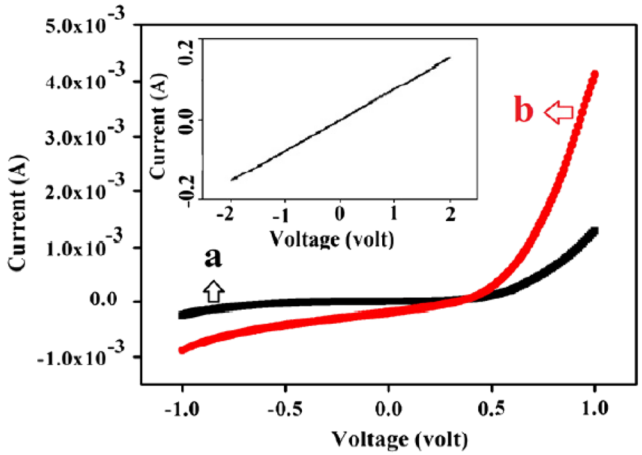

FIG. 10. I-V curves of the Cu_2O/TiO_2. Reprinted with permission from Hussain *et al.*, Thin Solid Films **522**, 430–434 (2012). Copyright 2012 Elsevier.

were prepared by electrodeposition using an aqueous $CuSO_4$ solution. To create solar cells, indium was evaporated onto the Cu_2O to form an electrode. Finally, the solar cells were annealed in air at 120 and 220 °C for 30 min. The PV curves were measured by irradiating the indium-tin oxide side of the cell with a solar simulator (~100 mW/cm^2, AM 1.5). The PV characteristics were as follows: $V_{oc} = 0.22$ V, $I_{SC} = 0.57$ mA/cm^2, FF = 0.45, and efficiency = 0.056% before annealing, and the authors achieved a conversion efficiency of ~0.11% after annealing at 120 °C. Ichimura and Kato[106] concluded that the low efficiency was due to poor quality copper oxide. They proposed that increasing the conversion efficiency of the cell could be improved by improving the crystallinity of copper (I) oxides by avoiding the formation of copper (II) oxide, and by annealing in reduced ambient O_2 pressure and at high temperatures.[106] Figure 12 shows the I–V curves in the dark and light (a) before annealing and (b) after annealing the TiO_2/Cu_2O.

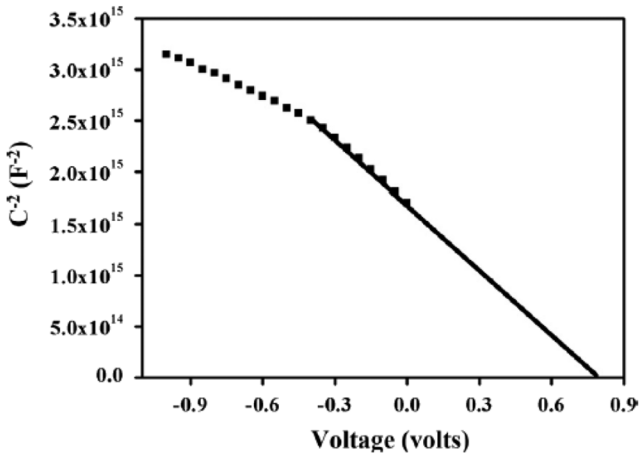

FIG. 11. C^{-2}–V curve of Cu_2O/TiO_2. Reprinted with permission from Hussain *et al.*, Mater. Sci. Semicond. Process. **25**, 181–185 (2014). Copyright 2014 Elsevier.

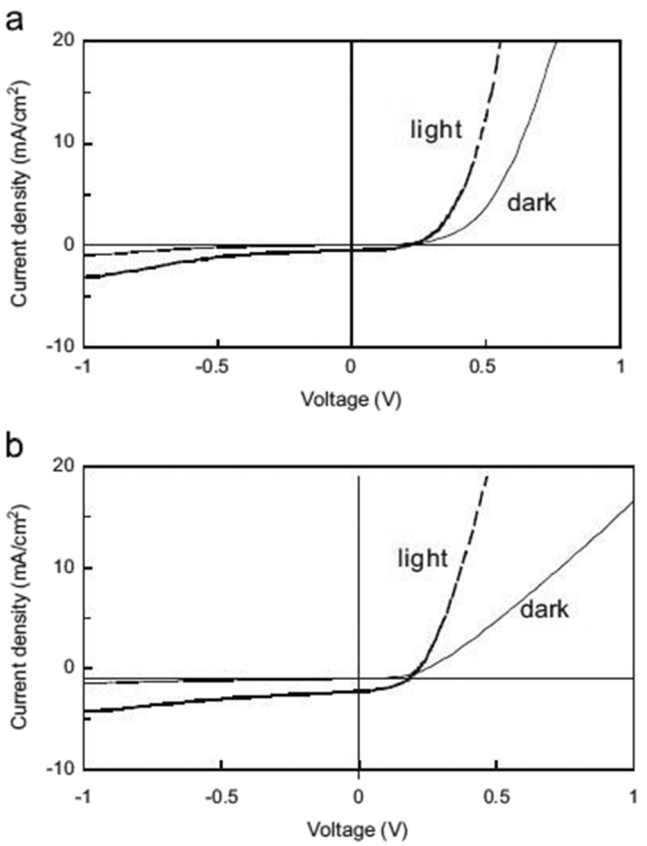

FIG. 12. I–V characteristics in the dark and light for the TiO_2/Cu_2O (a) before annealing and (b) after annealing. Reprinted with permission from M. Ichimura and Y. Kato, Mater. Sci. Semicond. Process. **16**(6), 1538–1541 (2013). Copyright 2013 Elsevier.

Luo *et al.*[173] manufactured Cu_2O/TiO_2 in two steps. TiO_2 nanorod films were deposited on glass covered FTO using a hydrothermal reaction. The TiO_2 layer was also below a compact layer beneath the nanorod layer. Next, a Cu_2O thin film was electrodeposited onto the TiO_2 nanorod structure. The electrodeposition time for the Cu_2O films was varied (20 min, 25 min, 30 min, 50 min, and 60 min) under −0.5 V. Finally, a gold layer was sputtered on top to form the contact electrode of each solar cell. The J-V curves of the heterojunction solar cells were investigated in the dark and under irradiation (1 Sun, 100 mW/cm^2) at room temperature. The highest conversion efficiency of this Cu_2O/TiO_2 solar cell was 1.25%, which was achieved after a Cu_2O film electrodeposition time of 30 min.[173]

Sawicka-Chudy *et al.*[32] produced a TiO_2/Cu_2O thin-film heterojunction solar cell using a DC magnetron-sputtering technique. They analyzed the I-V characteristics, optical characteristics, composition, and morphology, and performed atomic force microscopy and XRD analyses of the TiO_2/Cu_2O. To create solar cells, Au contacts were adhered to the copper oxide and indium tin oxide using conductive glue. The I–V curves of TiO_2/Cu_2O were measured in the dark and under illumination using a halogen lamp as the light source at 800 W/m^2. One of the TiO_2/Cu_2O heterojunctions was photosensitive, but exhibited no PV activity.[32]

Recently, Suleiman *et al.*[174] fabricated FTO-TiO_2/Cu_2O-Cu and FTO-ZnO/Cu_2O-Cu solar cells. Copper oxide films were electrodeposited on sprayed ZnO and TiO_2 structures. The authors analyzed the compositional, optical, and electrical properties. The PV characteristics for the FTO-TiO_2/Cu_2O-Cu were as follows: circuit current density (J_{SC}), 5.8 $\mu A/cm^2$; V_{oc}, 0.03 V; and efficiency, 0.037% and those for FTO-ZnO/Cu_2O-Cu were as follows: J_{SC}, 0.093 $\mu A/cm^2$; V_{oc}, 0.0364 V; and efficiency, 0.0076%. The FTO-TiO_2/Cu_2O-Cu solar cells had better efficiency than the FTO-ZnO/Cu_2O-Cu solar cells.[174]

Table IV summarizes the PV characteristics, thickness, thin-film fabrication methods, and contact(s) for copper oxide and TiO_2-based solar cells.

V. COMBINATION OF COPPER OXIDE WITH OTHER MATERIALS

Here, we briefly discuss and explain the available combinations of copper oxides with other materials that can be used as solar cells. These materials and combinations are as follows: Cu_2O/ZnO, Ga_2O_3/Cu_2O, and CuO/Si.

Minami *et al.*[175] produced Al-doped ZnO (AZO)/nondoped ZnO (ZO)/Cu_2O solar cells. Copper oxide sheets were manufactured by oxidizing the Cu sheets with a heat treatment process and ZO and AZO, and fabricated using a pulsed laser deposition method. The ohmic electrode on the back surface of Cu_2O was Cu_2S or Au. The authors studied the influence of the thickness of ZO thin-films ranging from 0 to 150 nm on V_{oc}, J_{SC}, FF, and efficiency. They showed that the efficiency of AZO/ZO/Cu_2O solar cells was greater than 3% (3.83%) for a n-ZO thin-film layer with a 30–50 nm thickness. Other PV parameters were J_{SC} = 0.69 mA/cm^2 and FF = 0.55.[175]

Lee *et al.*[64] demonstrated Ga_2O_3/Cu_2O heterojunction devices with a 10-nm-thick Ga_2O_3 buffer layer and *p*-type absorber Cu_2O (thickness: 2.5 μm). The bottom electrode was a 200-nm-thick layer of Au. The device had a 1-μm-thick Al top-electrode grid and a 95-nm-thick MgF_2 antireflective layer. The PV characteristics were as follows: V_{oc} = 1.2 V, J_{SC} = 7.3 mA/cm^2, FF = 44.7%, and efficiency 3.97%. They also studied the temperature dependence of the J–V characteristics and concluded that the "dominant recombination process occurs near the Ga_2O_3/Cu_2O interface."[64]

Masudy-Panah *et al.*[176] produced *p*-CuO(Ti)/*n*-Si solar cells by sputter deposition at room temperature and rapid thermal annealing. They studied the impact of Ti-doped copper (I) oxide on the PV properties. The Ti concentration varied from ~0.049 to ~0.598%. The potential of Ti doping for improving the PV properties and conductivity of CuO devices was analyzed. They investigated CuO(Ti) thin-films using atomic force microscopy, Raman spectroscopy, XRD, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, and the I-V characteristics of *p*-CuO(Ti)/*n*-Si heterojunction solar cells. The efficiency of *p*-CuO(Ti)/*n*-Si varied from 0.06% to 0.39%. The highest efficiency was 0.39%, which was achieved with a Ti concentration of 0.099.[176]

TABLE IV. Photovoltaic characteristics of TiO_2/Cu_2O, TiO_2/CuO solar cells.

Device structure	Reference	Method of fabrication	I_{SC} (mA)	J_{SC} (mA/cm^2)	V_{oc} (mV)	FF (-)	η (%)	Thickness of layers	Electrodes
Cu_2O/TiO_2	162	Electrodeposited Cu_2O, TiO_2 deposited by physical vapor deposition	[a]	0.70	460	[a]	[a]	TiO_2 0.1 μm	Ag/AgCl (reference electrode) platinum wire (counter electrode)
Cu_2O/TiO_2	173	Electrodeposited Cu_2O, TiO_2 hydrothermal reaction	[a]	8.91	364	~0.39	1.25	Cu_2O ~1.5 μm	Au electrode
Cu_2O/TiO_2	47	(rf) magnetron sputtering -TiO_2 electrodeposition -Cu_2O	[a]	0.001 27	340	~0.36	~0.15	TiO_2 0.1 μm, Cu_2O ~7 μm	Platinum foil -counter electrode, reference electrode -Ag/AgCl (4 M KCl)
Cu_2O/TiO_2	106	TiO_2-sol solution, Cu_2O -electrodeposition	Before annealing:					TiO_2 – 0.4, 0.5, 0.6 μm, Cu_2O – 0.5 μm	Counter electrode- Pt sheet (1.8 cm separation)
			[a]	0.57	220	0.45	0.056		
			After annealing:						
			[a]	1.34	180	0.46	0.11		
Cu_2O/TiO_2	9	Spray pyrolysis	[a]	0.40	350	0.25	[a]	TiO_2 – 0.06–0.32 μm, Cu_2O – 0.18–0.58 μm	Ag back contacts, FTO –front electrode
	171	TiO_2 nanotube arrays—anodization process, Cu_2O—electrodeposition	Before annealing:					[a]	TiO_2 nanotubes -working electrode, Ag/AgCl reference electrode, platinum wire counter electrode, 10 nm Au - top contact electrode
			[a]	0.10–0.33	90–250	~0.27	[a]		
			After annealing at 200 °C for 1 h					[a]	
			[a]	0.33	100	0.27	~0.01		
Cu_2O/TiO_2	128	TiO_2 - squeegee method, Cu_2O electrochemical deposition	[a]	0.003 1	470	[a]	0.0005	TiO_2 – 16 μm	Indium -top electrode, FTO bottom electrode
TiO_2/Cu_2O	174	Cu_2O- electrodeposition sprayed - TiO_2	[a]	0.005 8	30	[a]	0.037	TiO_2 – 0.04 μm	Graphite rod- counter electrode, Ag/AgCl - reference electrode
$Cu(NO_3)_2{\cdot}3H_2O$-containing TiO_2	169	Spray and electroplating	After treatment by electroplating					[a]	[a]
			0.31	[a]	430	0.31	0.35		
			After NaOH post-treatment and treated by electroplating						
			0.43	[a]	900	0.34	1.24		

TABLE IV. (*Continued.*)

Device structure	Reference	Method of fabrication	I_{SC} (mA)	J_{SC} (mA/cm^2)	V_{oc} (mV)	FF (-)	η (%)	Thickness of layers	Electrodes
TiO_2/CuO			0.08	[a]	620	0.33	0.14		
	60	Fix current electroplating and spray method	With electroplating process 20 s and with constant electroplating current of 10 mA					[a]	FTO, copper rod
TiO_2/CuO/Cu			0.72	…	640	0.42	1.62		

[a]No data.

Masudy-Panah *et al.*[177] produced *p*-CuO/*n*-Si by using rapid thermal annealing methods and conventional sputtering. They studied the influence of thermal treatment and working pressure during deposition on the PV properties of copper-oxide based devices. The highest efficiency achieved was 1.0%, V_{oc} = 4.9 V, J_{SC} = 6.4 mA/cm^2, and FF = 32% for solar cells annealed at 300 °C for 1 min. They concluded that the quality of the crystalline structure and interface might be improved and the carrier recombination rate reduced by increasing the working pressure during deposition.[177]

VI. THICKNESS OF COPPER OXIDE THIN-FILMS

The thickness of the copper oxide layers plays a key role in the conversion efficiency of copper oxide-based solar cells due to the discrepancy between the optical absorption length and copper oxide thickness. The thickness of copper oxide thin films influences the charge carrier transport properties and light absorption.[178]

Musselman *et al.*[179] studied the thickness of copper (I) oxide thin films in nanowire and bilayer Cu_2O-ZnO solar cells. They investigated the influence of Cu_2O thickness on V_{oc}, J_{SC}, and η. The thickness of the Cu_2O layer varied from 2 to 4.5 μm for bilayer solar cells and from 2 to 3.5 μm for nanowire solar cells. The highest efficiency was ~0.6% for bilayer solar cells and ~0.38% for nanowire solar cells with Cu_2O-ZnO layer thicknesses ranging from approximately 2.7 to 3.0 μm.[179]

Masudy-Panah *et al.*[178] sputtered the CuO films for photoelectrochemical water splitting with different film thicknesses, ranging from 0.2 to 0.7 μm. They observed that increasing the thickness of the Cu_2O layer from 0.2 to 0.7 μm increased the photocurrent. Increasing the Cu_2O layer thickness above 0.7 μm, however, degraded the photocurrent. They also attributed the initial increase in the photocurrent to the improvement in the light absorption capabilities of the thicker CuO thin films as well as an increase in recombination.[178] The authors proposed an optimum thickness of ~0.55 μm, which produced a photocurrent of 1.68 mA/cm^2 at 0 V.[178]

VII. CONCLUSION

In summary, we presented the main properties of TiO_2, cuprous oxide (Cu_2O), and cupric oxide (CuO); their potential applications, and, to the best of our knowledge, all of the solar cells based on copper oxide and TiO_2. Additionally, we provided a short review of the combination of copper oxide with other materials: Cu_2O with ZnO, CuO with ZnO, Ga_2O_3/Cu_2O, and CuO with Si, and the influence of the thickness of copper oxide layers on efficiency.

We compared the PV characteristics of solar cells, thicknesses of copper oxide and titanium layers, and electrodes to created heterojunctions. The highest energy conversion was for a TiO_2/CuO/Cu solar cell—1.62% produced by spray (TiO_2) and a fixed current electroplating method (Cu_2O). The efficiency results of the cells based on copper oxides are low compared with the theoretical results. To improve their performance, some researchers have proposed the following: increase the crystallinity of Cu_2O,[106] avoid the formation of copper oxides other than copper (I) oxide or copper (II) oxide, avoid defects at the heterojunction interface,[171] avoid an excessively thick copper oxide layer,[171] and use textured electrodes and antireflective coatings.[171] Moreover, avoiding "band discontinuity at the interface edges",[47] synthesizing larger and

higher quality copper oxide grains, reducing conduction band off set at the TiO_2/Cu_2O interface,[9] and increasing transmission of the top electrode may improve the efficiency.[171] Finally, using a NaOH post-treatment will help to improve the contact between the electrolyte, aluminum, and the thin films.[60]

This manuscript is intended as a review of the major literature to acquaint the readers with experimental results, and some general and theoretical principles of thin-film solar cells.

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