Microwave Assisted Preparation of Barium Doped Titania (Ba/TiO\(_2\)) as Photoanode in Dye Sensitized Solar Cells

Awais Ahmad \(^1\), Safia Khan \(^2\), Mariam Khan \(^3\), Rafael Luque \(^1,\,*\), Mohammed Jalalah \(^4,\,^5\) and Mabkhoot A. Alsaiari \(^4,\,^6,\,*\)

1. Introduction

Society needs green and cost-effective technologies for the energy sector owing to the global greenhouse effect and depletion of fossil fuels in recent years. Among all existing green energy technologies such as wind turbines, fuel cells, hydropower, tidal power, solar thermal and biomass, solar cells are considered among the most promising and prominent energy sources [1–5]. Dye-sensitized solar cells (DSSCs) constitute an advanced generation of solar cells that mimic natural photosynthesis. With fabrication techniques including solution processable methods, the use of cheap materials and decent power conversion efficiency (PCE), DSSCs are promising candidates for the conversion of solar light into electricity [6–8]. The highest PCE of 13% has been achieved in DSSCs by employing ruthenium as a light-absorbing material [9]. Techniques employed to improve the performance of DSSCs aim to minimize recombination of the photoinduced electron hole pair while improving the charge transfer rate of photo-generated electrons in the transparent conducting substrate [10]. Reducing the charge recombination and enhancing charge transfer can be achieved by optimizing the band gap of the semiconducting metal oxide (MOS). The MOS in a DSSC serves as a substrate for dye uplifting as well as provides a path for photoinduced charge generation [11,12].

TiO\(_2\) nanostructures are one of the significant photoanode materials owing to their superior properties, including wide band gap, large surface area, non-toxicity, low cost
and high stability [13,14]. The morphology of MOS plays a significant role in DSSCs; therefore, a fine-tuned morphology is required to deliver improved PCE in the device [15]. The photocatalytic efficiency of TiO$_2$ is affected by its ability to respond to radiation (UV along with visible light), and thus could be improved by shifting its optical absorption from UV to the visible region. It has been observed that the photocatalytic efficiency of TiO$_2$ is enhanced by modifying its band gap with different dopants [16]. A variety of TiO$_2$ nano-compositions involving nanoparticles, carbon spheres, TiO$_2$ nanoparticle composites, TiO$_2$ micro tablets, hollow spheres, nanotube composites, and nano-fiber nanoparticle composites have been successfully synthesized and used as DSSC photoanode materials [17–20]. Doping with transition metals [21,22], rare-earth elements [23,24] and noble metals [25] into TiO$_2$ has been widely investigated to reduce TiO$_2$ particle size and improve its (photo)(electro)catalytic performance. Co-doping along with different doping agents including metal–nonmetal, nonmetal–nonmetal, and metal—metal synergistically improves the optical absorption towards the visible region and reduces the recombination process [26]. Cu-N, B-N, Fe-C, Fe-N, Ni-N, and V-N have been studied as co-dopants with TiO$_2$ [27–33]. Co-doping of TiO$_2$ with N-C has been reported to modify its band gap, enhancing its photocatalytic activity towards the visible spectrum [34]. Co-doping of titania nanowires with tungsten carbon improves their electrochemical activity towards the oxygen-evolution reaction (OER) [35]. Ag/V-TiO$_2$ was also studied to photo-catalyze the degradation of rhodamine B dye in aqueous solutions. These co-doped materials exhibited the highest photocatalytic activity in the UV-visible region [36]. Similarly, it has also been previously reported that barium doping in TiO$_2$ nanoparticles using microwave irradiation increases the optical band gap and reduces the particle size of TiO$_2$ nanoparticles for microbiological activity [37]. Several studies have reported co-doping of TiO$_2$ to enhance its optoelectrical properties.

The present work deals with the preparation of TiO$_2$ and Ba/TiO$_2$ composites using a simple microwave irradiation method. Microwave-assisted swift heating has achieved substantial significance as an emerging and favorable method for one-pot preparation of different metal nanostructures. Structural, optical, morphological, elemental, and electrochemical behaviors of synthesized photoanodes materials are investigated by X-ray diffraction (XRD), UV-visible spectroscopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and electrochemical-impedance spectroscopy (EIS). Moreover, the photovoltaic performance of synthesized TiO$_2$ and Ba/TiO$_2$ photoanodes has been studied. Increasing the optical band gap and surface area of Ba/TiO$_2$ photoanodes led to a reduction of dark current and increased dye loading capacity [38]. DSSCs prepared using Ba/TiO$_2$ composite photoanode delivered a PCE of 2.34%.

2. Materials and Methods

2.1. Materials

Titanium (IV) isopropoxide TTIP (95% purity), ruthenium dye (N3 dye), polyethylene glycol (PEG), barium chloride and Triton X-100 were purchased from Alfa Aesar Company India. Ethanol was purchased from Merck Company India. Chloroplatinic acid (99.9%) was purchased from Himedia Company India. All of these chemicals were utilized as received, without any further treatments. All of the solutions were prepared using deionized water (DI).

2.2. Preparation of TiO$_2$ and Ba/TiO$_2$ Photoanode

A facile microwave irradiation method was employed to prepare Ba$_{(0.5)}$TiO$_2$ photoanode materials. An initial solution was prepared using 2 g of TTIP added with 60 mL of deionized water and stirred for 1 h at 100 °C. A separate solution was prepared using barium chloride dissolved in DI water. After that, both solutions were mixed and kept under stirring for 1 h at room temperature. The solution was kept under microwave irradiation for 5 min at 450 W. The advantage of using a microwave oven relates to a reduced synthesis time and energy consumption as compared to conventional heating. Microwaves provide homogeneous and rapid heating [39]. Afterwards, the obtained photoanode materials were
calcined at 500 °C for 1 h to enhance the crystalline nature of the photoanode material. The same procedure was adopted for the preparation of TiO₂ photoanode.

2.3. Photoanode Preparation

Fluorine-doped tin oxide (FTO) glass substrates were cleaned in a soap solution followed by distilled water and ethanol. Hereafter, the synthesized photoanode material was prepared using binder solutions of PEG and Triton X100. As prepared, Ba/TiO₂ was deposited onto FTO using the doctor blade technique. The coated substrate was sintered at 300°C for 1 h to evaporate the binder as well as to generate porosity in the materials. The sintered substrate was immersed into 0.5 mM of ruthenium dye solution for 24 h to absorb the dye molecule. A thin layer of platinum was deposited onto the FTO glass using 5 mM chloroplatinic acid via doctor blade technique. The photo-electrode was clamped (using binder clips) with the counter-electrode to produce a sandwich-type formation. The liquid redox electrolyte composed of 0.5M potassium iodide (KI) and 0.02 M iodine (I₂) dissolved in acetonitrile was filled between the photoelectrode and counter-electrode. The active surface area of the as-prepared DSSC was about 0.25 cm² and the cross-sectional area of TiO₂ and Ba/TiO₂, approx. 10 µm.

2.4. Characterization

X-Ray diffraction (PANalytical-X’pert Pro powder diffractometer λ = 1.54 Å using Cu Kα radiation) analysis was conducted to determine the crystal structure of the MOS with 2θ range values from 10° to 80°. The measurement was carried out by step size of 0.0170° up to four decimal accuracies. SEM (ZEIS EVO 18 instrument with 20 kV acceleration voltage and 1.30 K magnification) was used for the morphological studies of the of photoanode materials. UV-visible spectrophotometry (Perkin-Elmer-Lambda-35 spectrophotometer) was used to investigate the optical properties. EIS was conducted by VSP300 biological instrument with a 10 mV voltage amplitude in the frequency range of 1 MHz–1 Hz. The current voltage (I-V) measurement was observed by means of an electrochemical computer-controlled workstation as well as a SAN-EI solar-stimulator. A 150-watt xenon lamp was used as a light source with an AM 1.5 G filter and an intensity of 100 mW cm⁻².

3. Results and Discussions

3.1. Structural Analysis

XRD patterns of single TiO₂ as well as Ba/TiO₂ nanomaterials are displayed in Figure 1. The diffraction peaks of TiO₂ and Ba/TiO₂ nanomaterials at 2θ values were 25.09°, 37.65°, 47.89°, 53.89°, 55.07°, 62.40°, 70.04°, and 75.00°, matching well with JCPDS data (21-1272) having (101), (004), (200), (105), (211), (204) crystal planes, respectively [26]. No other characteristic peaks were reflected in the XRD pattern. Hence, both samples exhibited tetragonal structure, and corresponding lattice constant values are shown in Table 1. In the case of Ba/TiO₂ nanomaterials, an increase in intensity was evidenced due to the incorporation of Ba²⁺ (1.42 nm) into the TiO₂ host lattice because the ionic radius of Ba²⁺ is greater than that of Ti⁴⁺ (0.74 nm), which resulted in an increase in crystallinity. This substitution caused lattice distortion, inflation of the TiO₂ nanocrystal, and internal stress due to Ba doping [40], which reduced nucleation growth (particle size controller) [41]. Another study showed that doping of substrates with Ba caused shrinkage of the crystallite size of modified nanomaterials [42].

| Photocatalytic Material | FWHM (2θ) | d-Spacing (Å) | Crystallite Size(D) (nm) | Lattice Constant (Å) | Unit Cell Volume V (Å³) | Density (ρ) (g/cm³) | Specific Surface Area (m²/g) |
|------------------------|------------|----------------|-------------------------|----------------------|-----------------------|---------------------|-----------------------------|
| TiO₂                   | 0.568 ± 0.026 | 3.494          | 25                      | 3.778 ± 0.005        | 9.480 ± 0.012         | 135.31              | 3.9                        | 61                         |
| Ba/TiO₂                | 0.876 ± 0.038 | 3.504          | 16                      | 3.781 ± 0.002        | 9.470 ± 0.004         | 135.38              | 3.9                        | 95                         |
where, \( d \) is the \( d \)-spacing between two consecutive lattices observed from XRD, \((h,k,l)\) indicate the miller indices, \( t \) is the crystallite size, \( \beta \) is the full width at half maximum, \( a, b \), and \( c \) display as lattice constant for \( \text{TiO}_2 \), \( \rho \) is the density of the prepared sample, \( \lambda \) indicates the wavelength of the X-ray radiation used, and \( \theta \) refers to the diffraction angle;

\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} 
\]

\[
t = \frac{0.9\lambda}{\rho \cos \theta} 
\]

where \( d \) is the density of the prepared sample, \( n \) is 4 for anatase phase \( \text{TiO}_2 \) and 2 for rutile phase \( \text{TiO}_2 \), \( M \) is the molecular weight of the prepared nanomaterials, \( N \) corresponds to Avogadro’s constant value, \( V \) is the volume of the prepared nanomaterials, and \( S_a \) states the specific surface of the prepared sample. Table 1 shows the calculated structural values derived from the XRD patterns of \( \text{TiO}_2 \) and \( \text{Ba/TiO}_2 \) nanomaterials. The average crystallite sizes estimated were 25 nm for single \( \text{TiO}_2 \) and 16 nm for \( \text{Ba/TiO}_2 \) nanomaterials, respectively. When Ba ions were doped into the \( \text{TiO}_2 \) lattice, a decrease in nucleation (and subsequent growth rate) was observed for \( \text{TiO}_2 \) nanomaterials, leading to a reduction in particle size of \( \text{Ba/TiO}_2 \). The reduction in particle size increases the surface area of \( \text{TiO}_2 \). The specific surface area of \( \text{TiO}_2 \) (61 m²/g) was smaller than that of \( \text{Ba/TiO}_2 \) (95 m²/g). This favored dye adsorption in the photo electrode, thereby improving photovoltaic performance in the DSSC.

3.2. Optical Properties

Figure 2 represents the UV-visible spectra of \( \text{TiO}_2 \) and \( \text{Ba/TiO}_2 \) photoanode materials. \( \text{Ba/TiO}_2 \) exhibited a significant visible absorption above 400 nm, which was an indication of changes occurring in the optical absorption of \( \text{TiO}_2 \) photoanode material due to metal doping. Peak edges of \( \text{Ba/TiO}_2 \) photoanode showed some regular and trivial blue shifts.
comparative to TiO$_2$ photoanode. The blue shift was attributable to the Burstein–Moss effect, leading to the movement of Fermi level towards the conduction band due to an increase in electron concentration because of Ba doping [44,45]. It is very useful to increase the photocurrent density and also the charge transfer resistance of synthesized photoanodes. The absorption of TiO$_2$ and Ba/TiO$_2$ were at 415 nm and 400 nm, respectively.

![Figure 2](image-url)

**Figure 2.** UV-visible spectra of synthesized TiO$_2$ and Ba/TiO$_2$ photoanodes.

Optical band gap values were determined by using Tauc plots as presented in Figure 3a. Ba/TiO$_2$ photoanode (3.26 eV) has a higher band gap value compared to TiO$_2$ photoanode (3.21 eV) because of quantum confinement effects observed due to the smaller size of as-synthesized samples. According to the theory of quantum efficiency, the holes of valence band and conduction band electrons are confined by the potential barrier of the surface. As a result, the band gap energy is increased with decreasing size of synthesized particles [46,47]. The increase in band gap of doped TiO$_2$ can be interpreted in terms of Mott’s transition effect and Burstein–Moss (BM) effects. According to Mott’s criteria, the band gap of the donor combines with the conduction band of the host material [48], while BM effects present a relationship between the band gap and concentration of carriers [49,50], as given below:

$$E_g^{BM} = \frac{h^2}{2\lambda m_e} \left( \frac{3\pi^2 N_c}{\lambda} \right)$$

(5)

where $\lambda$, $h$, and $m_e$ are the effective reduced mass of TiO$_2$, Planck’s constant and the electron free mass, respectively. According to the BM effect, the carrier density of semiconductors increases with Ba doping, which causes the Fermi level to shift into the conduction band [51]. Due to this doping, the low energy transition is clogged, and broadening in the band gap takes place [52]. This novel effect of Ba doping on optical properties can pave the way to its extended use in optoelectronic and photovoltaic applications.

The value of $n$ coefficient is determined by the Tauc relationship (Equation (6)). The $n$ coefficient is related to the possible transition of electrons. For indirect allowed electronic transition, its value is 2 and 3 for indirect forbidden transitions.

$$a\hbar \theta = A (\hbar \theta - E_g)^n$$

(6)

$$n = \frac{\ln \left( a\hbar \theta \right)}{\ln (\hbar \theta - E_g)}$$

(7)
where $\alpha$ is the absorption coefficient, $h$ is Plank’s constant, and $A$ is absorption constant [53]. From the slope of $\ln F(R)$ vs. $\ln (h\nu - E_g)$, the value of $n$ is determined. The result listed in Table 2 represents the approximated value of $n = 2$ for TiO$_2$ and Ba/TiO$_2$ which is in agreement with values in the literature for TiO$_2$, which is an indirect semiconductor [54].

![Figure 3](image-url)  
**Figure 3.** (a) Tauc plots of synthesized TiO$_2$ and Ba/TiO$_2$ photoanodes (b) Graphical representation of Equation (7), inset relates to Ba/TiO$_2$.

**Table 2.** $n$ coefficient determination and band gap.

| Sample     | $E_g$ (eV) | $n$ Coefficient |
|------------|-----------|-----------------|
| TiO$_2$    | 3.21      | 1.72 ± 0.003    |
| Ba/TiO$_2$| 3.26      | 1.61 ± 0.003    |

Figure 4 presents the UV-visible absorption spectrum of dye molecule-adsorbed TiO$_2$ and Ba/TiO$_2$ photoanodes. The Ba/TiO$_2$ photoanode had high absorption compared to the TiO$_2$ photoanode. The increased absorption was due to the increasing surface area of the Ba/TiO$_2$ photoanode, which was also confirmed by XRD results. This behavior enhances photocurrent density in DSSCs. Moreover, the shift in wavelength in the visible region further supported our findings as productive in DSSCs, because the photocatalytic efficiency of TiO$_2$ is affected by its ability to respond to UV radiation along with visible light, which could be improved by shifting its optical absorption from UV to the visible region. Ba doping increased the absorption in the visible region.

![Figure 4](image-url)  
**Figure 4.** UV-visible absorption spectra of synthesized TiO$_2$ and Ba/TiO$_2$ photoanodes with N3 dye molecule.
3.3. Morphological Studies

The surface morphologies of the TiO\textsubscript{2} and Ba/TiO\textsubscript{2} nanostructures were subsequently examined by SEM as shown in Figure 5. Both TiO\textsubscript{2} (5a) and Ba/TiO\textsubscript{2} (5b) exhibited similar agglomerated spherical shape particles. In terms of chemical composition, TiO\textsubscript{2} nanostructures contained Ti and O, only, which confirmed that the material was free from impurities, as observed from Figure 5c. The presence of Ba was confirmed in the Ba/TiO\textsubscript{2} nanostructures from Figure 5d.

![Figure 5. SEM analysis of synthesized (a) TiO\textsubscript{2} and (b) Ba/TiO\textsubscript{2}, and EDS analysis of synthesized (c) TiO\textsubscript{2} and (d) Ba/TiO\textsubscript{2} nanopowders.](image)

3.4. Electrochemical Behavior of TiO\textsubscript{2} and Ba/TiO\textsubscript{2}

The reaction kinetics linked with DSSCs were investigated using EIS results. EIS spectra of TiO\textsubscript{2} and Ba/TiO\textsubscript{2} photoanodes under dark conditions with 0.6 V open circuit voltage are depicted in Figure 6. The EIS of DSSC was explained by three semicircles in the high, middle, and low frequency range, corresponding to the electrochemical output in platinized counter-electrode and electrolyte-interface (R\textsubscript{1}), WE/electrolyte (R\textsubscript{2}), and diffusion resistance of electrolyte (R\textsubscript{d}), respectively. The displacement of the graph from origin represents the series resistance due to the contact resistance of the cell (R\textsubscript{s}) [55]. Associated charge transfer in the electrolyte influenced the low frequency region, which was evident from the third semicircle. From the fitted data, the Ba/TiO\textsubscript{2} photoanode charge transfer resistance value was higher than the TiO\textsubscript{2} photoanode charge transfer resistance value. Barium doping increased the band gap value (which was also confirmed by optical analysis), and this reduces electron recombination in the Ba/TiO\textsubscript{2}/electrolyte interface. This behavior is attributed to the charge transfer value increment. The increment of charge transfer resistance was helpful to reduce charge recombination, which was evident for the photocurrent increment.
which led to enhanced dye-loading capacity. These results were also confirmed by the XRD and UV analysis. Another important factor was that the increment in photocurrent density was supported by the recombination rate or dark current reduction. The Ba/TiO\textsubscript{2} photoanode had the high recombination resistance compared to the TiO\textsubscript{2} photoanode, which reduce dark current production between the MOS and electrolyte.

### 3.5. Photovoltaic Studies

The photovoltaic performance of the fabricated DSSC is shown in Figure 7. Photocurrent density of Ba/TiO\textsubscript{2} was higher than that of the TiO\textsubscript{2} photoanode. This increment was due to the increased photon absorption of dye molecule as compared to the TiO\textsubscript{2} counterpart. The Ba/TiO\textsubscript{2} photoanode had higher surface area than the TiO\textsubscript{2} photoanode, which led to enhanced dye-loading capacity. These results were also confirmed by the XRD and UV analysis. Another important factor was that the increment in photocurrent density was supported by the recombination rate or dark current reduction. The Ba/TiO\textsubscript{2} photoanode had the high recombination resistance compared to the TiO\textsubscript{2} photoanode, which reduce dark current production between the MOS and electrolyte.

![Figure 6. EIS analysis of synthesized (a) TiO\textsubscript{2}, (b) Ba/TiO\textsubscript{2} photoanode and along with the equivalent circuit of corresponding EIS.](image)

![Figure 7. Photovoltaic response of synthesized TiO\textsubscript{2} and Ba/TiO\textsubscript{2} photoanodes.](image)
The Ba/TiO$_2$ photoanode yielded higher PCE (3.4%) compared to the TiO$_2$ photoanode (2.1%). The calculated photovoltaic parameters are summarized in Table 3. The higher PCE of the Ba/TiO$_2$ photoanode (3.4%) corresponds to a maximum output power density ($P_{\text{max}}$) of approximately 34.4 $\mu$W/cm$^2$ as compared to the TiO$_2$ photoanode’s $P_{\text{max}}$ of 26.5 $\mu$W/cm$^2$. These findings suggest that DSSCs can be produced with the appropriate power rating to operate electronic devices such as tablets and Internet-of-Things gadgets that require low power $P_{\text{max}} < 100$ $\mu$W/cm$^2$ [56].

Table 3. Photovoltaic parameters derived from current voltage characteristic curves of synthesized TiO$_2$ and Ba/TiO$_2$ photoanodes.

| Sample   | Short Circuit Current Density $J_{\text{sc}}$ (mA/cm$^2$) | Open Circuit Voltage $V_{\text{oc}}$ (mV) | Fill Factor FF (%) | Efficiency (η) (%) | Ref          |
|----------|----------------------------------------------------------|------------------------------------------|-------------------|-------------------|--------------|
| TiO$_2$  | 5.96                                                     | 761                                      | 48                | 2.1               | Present work |
| Ba/TiO$_2$ | 8.70                                       | 740                                      | 53                | 3.4               | Present work |
| TiO$_2$  | 2.53                                                     | 650                                      | 63                | 1.03              | [57]         |
| W-TiO$_2$ | 4.77                                                    | 730                                      | 71                | 2.47              | [57]         |
| Fe-TiO$_2$ | 1.52                                                    | 680                                      | 0.463             | 0.47              | [26]         |

4. Conclusions

Incorporation of barium (0.5 wt%) into TiO$_2$ was successfully accomplished using a microwave irradiation method. With respect to Ba content, its incorporation modulated the band gap of TiO$_2$ by decreasing particle size, leads to increased specific surface area and consequently, superior dye uptake and high photocurrent, resulting in higher DSSC power conversion efficiency. The higher band gap value of Ba/TiO$_2$ (3.26 eV) as compared to TiO$_2$ photoanode (3.21 eV) was attributable to the quantum confinement effect, which was observed due to the reduced size of the as-synthesized samples. EDS results confirmed the presence of barium in Ba/TiO$_2$ without any impurities; this was further confirmed by XRD results. A higher efficiency of Ba/TiO$_2$ photoanode was observed as compared to pure TiO$_2$ (3.4 vs 2.1%). Barium doped titania (Ba/TiO$_2$) could be employed in DSSCs owing to its relevant photoactive properties, with further prospects for other applications including photocatalysis as well as wastewater treatment.

Author Contributions: Conceptualization, A.A. and S.K.; methodology, M.K.; software, M.K.; validation, M.K.; writing—original draft preparation, A.A.; writing—review and editing, R.L.; visualization, M.J.; supervision, R.L.; project administration, M.A.A.; funding acquisition, M.A.A. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by Najran University, and the grant number is NU/IFC/INT/01/003.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The authors would like to acknowledge the support of the deputy for research and innovation-Ministry of Education, Kingdom of Saudi Arabia for this research through grant (NU/IFC/INT/01/003) under the institutional funding committee at Najran University, Kingdom of Saudi Arabia.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Perera, F. Pollution from fossil-fuel combustion is the leading environmental threat to global pediatric health and equity: Solutions exist. Int. J. Environ. Res. Public Health 2018, 15, 16. [CrossRef] [PubMed]
2. Khan, S.; Shah, S.S.; Anjum, M.A.R.; Khan, M.R.; Janjua, N.K. Electro-oxidation of ammonia over copper oxide impregnated γ-Al2O3 nanocatalysts. Coatings 2021, 11, 313. [CrossRef]
3. Tiewsoh, S.L.; Jirásek, J.; Sivek, M. Electricity generation in India: Present state, future outlook and policy implications. Energies 2019, 12, 1361. [CrossRef]
4. Khan, M.; Janjua, N.K.; Khan, S.; Qazi, I.; Ali, S.; Saad Algharni, T. Electro-oxidation of ammonia at novel $\text{Ag}_2\text{O} - \text{PrO}_2 / \gamma - \text{Al}_2\text{O}_3$ catalysts. *Coatings* **2021**, *11*, 257. [CrossRef]

5. Saleem, M.; Irfan, M.; Tabassum, S.; Albaqami, M.D.; Javed, M.S.; Hussain, S.; Pervaiz, M.; Ahmad, I.; Ahmad, A.; Zubair, M. Experimental and theoretical study of highly porous lignocellulose assisted metal oxide photoelectrodes for dye-sensitized solar cells. *Arab. J. Chem.* **2021**, *14*, 102937. [CrossRef]

6. Ansir, R.; Shah, S.M.; Ullah, N.; Hussain, M.N. Performance of pyrocatechol violet and carminic acid sensitized $\text{ZnO}/\text{CdS}$ nanostructured photoactive materials for dye sensitized solar cell. *Solid-State Electron.* **2020**, *172*, 107886. [CrossRef]

7. Jacobson, M.Z.; Delucchi, M.A. Providing all global energy with wind, water, and solar power, Part I. Technologies, energy resources, quantities and areas of infrastructure, and materials. *Energy Policy* **2011**, *39*, 1154–1169. [CrossRef]

8. Irvine, S. Solar Cells and Photovoltaics. In *Springer Handbook of Electronic and Photonic Materials*; Springer: Cham, The Netherlands, 2017; p. 1.

9. Gul, M.; Kotak, Y.; Muneer, T. Review on recent trend of solar photovoltaic technology. *Energy Explor. Exploit.* **2016**, *34*, 485–526. [CrossRef]

10. Shih, K.; Workshop, S.; Watanabe, S. Dye-sensitized solar cells: Fundamentals and current status. *Nanoscale Res. Lett.* **2018**, *13*, 381. [CrossRef]

11. Bose, S.; Soni, V.; Genwa, K. Recent advances and future prospects for dye sensitized solar cells: A review. *Int. J. Sci. Res. Publ.* **2015**, *5*, 1–8.

12. Mátravölgyi, B.; Hergert, T.; Thurner, A.; Varga, B.; Sangiorgi, N.; Béndoni, R.; Zani, L.; Reginato, G.; Calamante, M.; Sinicropi, A.; et al. Synthesis and Investigation of Solar-Cell Photosensitizers Having a Fluorazone Backbone. *Eur. J. Org. Chem.* **2017**, *2017*, 1843–1854. [CrossRef]

13. Yu, Q.; Pang, Y.; Jiang, Q. NiS submicron cubes with efficient electrocatalytic activity as the counter electrode of dye-sensitized solar cells. *R. Soc. Open Sci.* **2018**, *5*, 180186. [CrossRef] [PubMed]

14. Carella, A.; Borbone, F.; Centore, R. Research progress on photosensitizers for DSSC. *Front. Chem.* **2018**, *6*, 481. [CrossRef] [PubMed]

15. Mishra, A.; Fischer, M.K.; Bäuerle, P. Metal-free organic dyes for dye-sensitized solar cells: From structure: Property relationships to design rules. *Angew. Chem. Int. Ed.* **2009**, *48*, 2474–2499. [CrossRef] [PubMed]

16. Momeni, M.M. Dye-sensitized solar cell and photocatalytic performance of nanocomposite photocatalyst prepared by electrochemical anodization. *Bull. Mater. Sci.* **2016**, *39*, 1389–1395. [CrossRef]

17. Su'ai, M.S.; Rahman, M.Y.A.; Ahmad, A. Review on polymer electrolyte in dye-sensitized solar cells (DSSCs). *Sol. Energy* **2015**, *113*, 452–470. [CrossRef]

18. Wang, H.; Hu, Y.H. Graphene as a counter electrode material for dye-sensitized solar cells. *Energy Environ. Sci.* **2012**, *5*, 8182–8188. [CrossRef]

19. Labat, F.; Ciuffini, I.; Hratchian, H.P.; Frisch, M.J.; Raghavachari, K.; Adamo, C. Insights into working principles of ruthenium polypyridyl dye-sensitized solar cells from first principles modeling. *J. Phys. Chem. C* **2011**, *115*, 4297–4306. [CrossRef]

20. Corrao, R.; D’Anna, D.; Morini, M.; Pastore, L. DSSC-integrated Glassblocks for the construction of Sustainable Building Envelopes. In *Advanced Materials Research*; Trans Tech Publ: Zurich, Switzerland, 2014.

21. Wu, C.-G.; Chao, C.-C.; Kuo, F.-T. Enhancement of the photo catalytic performance of $\text{TiO}_2$ catalysts via transition metal modification. *Catal. Today* **2004**, *97*, 103–112. [CrossRef]

22. Inturi, S.N.R.; Boningari, T.; Suidan, M.; Smirniotis, P.G. Visible-light-induced photodegradation of gas phase acetonitrile using aerosol-made transition metal (V, Cr, Fe, Co, Mn, Mo, Ni, Cu, Y, Ce, and Zr) doped TiO$_2$ nanorods using soft solution processing. *J. Appl. Phys.* **2012**, *112*, 144305. [CrossRef]

23. Chen, Y.; Wang, Y.; Li, W.; Yang, Q.; Hou, Q.; Wei, L.; Liu, L.; Huang, F.; Ju, M. Enhancement of photocatalytic performance with the use of noble-metal-decorated TiO$_2$ nanocrystals as highly active catalysts for aerobic oxidation under visible-light irradiation. *Appl. Catal. B Environ.* **2017**, *210*, 352–367. [CrossRef]

24. Momeni, M.M.; Akkarnia, M.; Ghayeb, Y. Preparation of S–W–codoped TiO$_2$ nanotubes and effect of various hole scavengers on their photoelectrochemical activity: Alcohol series. *Int. J. Hydrog. Energy* **2020**, *45*, 33552–33562. [CrossRef]

25. Wu, Y.; Zhang, J.; Xiao, L.; Chen, F. Properties of carbon and iron modified TiO$_2$ photocatalyst synthesized at low temperature and photodegradation of acid orange 7 under visible light. *Appl. Surf. Sci.* **2010**, *256*, 4260–4268. [CrossRef]

26. Sinhm, A.; Setia, H.; Kumar, V.; Sobti, A.; Toor, A.P. Enhanced photocatalytic activity of nickel and nitrogen codoped TiO$_2$ under sunlight. *Environ. Technol. Innov.* **2020**, *18*, 100658. [CrossRef]

27. Lu, W.C.; Nguyen, H.D.; Wu, C.Y.; Chang, K.S.; Yoshimura, M. Modulation of physical and photocatalytic properties of (Cr, N) codoped TiO$_2$ nanorods using soft solution processing. *J. Appl. Phys.* **2014**, *115*, 144305. [CrossRef]

28. Liu, R.; Yang, F.; Xie, Y.; Yu, Y. Visible-light-responsive boron and nitrogen codoped anatase TiO$_2$ with exposed [0 0 1] facet: Calculation and experiment. *Appl. Surf. Sci.* **2019**, *466*, 568–577. [CrossRef]
31. Jaiswal, R.; Bharame, J.; Patel, N.; Dashora, A.; Kothari, D.C.; Miotello, A. Copper and Nitrogen co-doped TiO$_2$ photocatalyst with enhanced optical absorption and catalytic activity. *Appl. Catal. B Environ.* 2015, 168, 333–341. [CrossRef]

32. Zhang, S. Synergistic effects of C–Cr codoping in TiO$_2$ and enhanced sonocatalytic activity under ultrasonic irradiation. *Ultrason. Sonochem.* 2012, 19, 767–771. [CrossRef]

33. Patel, N.; Jaiswal, R.; Warang, T.; Scardellui, G.; Dashora, A.; Ahuja, B.L.; Kothari, D.C.; Miotello, A. Efficient photocatalytic degradation of organic water pollutants using V–N-codoped TiO$_2$ thin films. *Appl. Catal. B Environ.* 2014, 150, 74–81. [CrossRef]

34. Trevisan, V.; Olivo, A.; Pinna, F.; Signoretto, M.; Vindigni, F.; Cerrato, G.; Bianchi, C.L. CN/TiO$_2$ photocatalysts: Effect of co-doping on the catalytic performance under visible light. *Appl. Catal. B Environ.* 2014, 160, 152–160. [CrossRef]

35. Cho, I.S.; Lee, C.H.; Feng, Y.; Logar, M.; Rao, P.M.; Cai, L.; Kim, D.R.; Sinclair, R.; Zheng, X. Codoping titanium dioxide nanowires with tungsten and carbon for enhanced photoelectrochemical performance. *Nat. Commun.* 2013, 4, 1723. [CrossRef]

36. Yang, X.; Ma, F.; Li, K.; Guo, Y.; Hu, J.; Li, W.; Guo, Y. Mixed phase titanium nanocomposite codoped with metallic silver and vanadium oxide: New efficient photocatalyst for dye degradation. *J. Hazard. Mater.* 2010, 175, 429–438. [CrossRef]

37. Devi, R.S.; Venckatesh, D.R.; Sivaraj, D.R. Synthesis of titanium dioxide nanoparticles by sol-gel technique. *Int. J. Innov. Res. Sci. Eng. Technol.* 2014, 3, 15206–15211. [CrossRef]

38. Vijayalakshmi, K.; Sivaraj, D. Synergistic antibacterial activity of barium doped TiO$_2$ nanoclusters synthesized by microwave processing. *RSC Adv.* 2016, 6, 9663–9671. [CrossRef]

39. Dahiya, M.S.; Tomer, V.K.; Duhan, S. Metal-ferrite nanocomposites for targeted drug delivery. In *Applications of Nanocomposites in Drug Delivery*; Elsevier: Amsterdam, The Netherlands, 2018; pp. 737–760.

40. Badawi, A.; Althobaiti, M.G.; Alharthi, S.S.; Al-Baradi, A.M. Tailoring the optical properties of CdO nanostructures via barium doping for optical windows applications. *Phys. Lett. A* 2021, 411, 127553. [CrossRef]

41. Patel, S.; Gajbhiye, N.; Date, K.S. Ferromagnetism of Mn-doped TiO$_2$ with enhanced optical absorption and catalytic activity. *Appl. Catal. B Environ.* 2014, 150, 74–81. [CrossRef]

42. AlFaify, S.; Ganesh, V.; Haritha, L.; Shkir, M. An effect of La doping on physical properties of CdO films facilely casted by spin coating for optoelectronic applications. *Phys. B: Condens. Matter* 2019, 562, 135–140. [CrossRef]

43. N’Kouon, K.; Lare, Y.; Haris, M.; Baneto, M.; Amou, K.A.; Napo, K. Influence of barium doping on physical properties of zinc oxide thin films synthesized by SILAR deposition technique. *Adv. Mater. 2014, 3*, 63–67. [CrossRef]

44. Cheng, G.; Xu, F.; Stadler, F.J.; Chen, R. A facile and general synthesis strategy to doped TiO$_2$ nanoaggregates with a mesoporous structure and comparable property. *RSC Adv.* 2015, 5, 64293–64298. [CrossRef]

45. Moss, T.S. The interpretation of the properties of indium antimonide. *Proc. Phys. Soc.* 1954, 67, 10. [CrossRef]

46. Singh, M.; Goyal, M.; Devlal, K. Size and shape effects on the band gap of semiconductor compound nanomaterials. *J. Taibah Univ. Sci.* 2018, 12, 470–475. [CrossRef]

47. Son, Y.; Park, M.; Son, Y.; Lee, J.S.; Jang, J.H.; Kim, Y.; Cho, J. Quantum confinement and its related effects on the critical size of GeO$_2$ nanoparticles anodes for lithium batteries. *Nano Lett.* 2014, 14, 1005–1010. [CrossRef] [PubMed]

48. Roth, A.; Webb, J.; Williams, D. Absorption edge shift in ZnO thin films at high carrier densities. *Solid State Commun.* 1981, 39, 1269–1271. [CrossRef]

49. Velusamy, P.; Babu, R.R.; Ramamurthi, K.; Elangovan, E.; Viegas, J. Effect of La doping on the structural, optical and electrical properties of spray pyrolytically deposited CdO thin films. *J. Alloy. Condens. Mater.* 2017, 339, 135–140. [CrossRef]

50. Kumar, R.C.; Rao, N.M.; Kaleemulla, S.; Rao, G.V. Structural, optical and magnetic properties of Sn doped ZnS nano powders prepared by solid state reaction. *Phys. B Condens. Matter* 2017, 522, 75–80. [CrossRef]

51. Sangiorgi, N.; Aversa, L.; Tatti, R.; Verucchi, R.; Sanson, A. Spectrophotometric method for optical band gap and electronic transitions determination of semiconductor materials. *Opt. Mater.* 2017, 64, 18–25. [CrossRef]

52. Reddy, K.M.; Manorama, S.V.; Reddy, A.R. Bandgap studies on anatase titanium dioxide nanoparticles. *Mater. Chem. Phys.* 2003, 78, 239–245. [CrossRef]

53. Yoo, K.; Kim, J.Y.; Lee, J.A.; Kim, J.S.; Lee, D.K.; Kim, K.; Kim, J.Y.; Kim, B.; Kim, H.; Kim, W.M.; et al. Completely transparent conducting oxide-free and flexible dye-sensitized solar cells fabricated on plastic substrates. *ACS Nano* 2015, 9, 3760–3771. [CrossRef] [PubMed]

54. Saeed, M.A.; Kang, H.C.; Yoo, K.; Asiam, F.K.; Lee, J.J.; Shim, J.W. Cosensitization of metal-based dyes for high-performance dye-sensitized photovoltaics under ambient lighting conditions. *Dye. Pigment.* 2021, 194, 106624. [CrossRef]

55. Amarsingh Bhabu, K.; Kalpana Devi, A.; Theerthagiri, J.; Madhavan, J.; Balu, T.; Rajasekaran, T.R. Tungsten doped titanium dioxide as a photoanode for dye sensitized solar cells. *J. Mater. Sci. Mater. Electron.* 2017, 28, 3428–3439. [CrossRef]