Article

Laser Sintering of TiO₂ Films for Flexible Dye-Sensitized Solar Cells

Huan Yang ¹, Wenwen Liu ², Changwen Xu ^{1,*} , Dianyuan Fan ¹, Yu Cao ² and Wei Xue ^{2,*}

¹ International Collaborative Laboratory of 2D Materials for Optoelectronics Science and Technology of Ministry of Education, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China; hylaser@gmail.com (H.Y.); fandy@cae.cn (D.F.)

² Zhejiang Key Laboratory of Laser Processing Robot, College of Mechanical and Electrical Engineering, Wenzhou University, Wenzhou 325035, China; sophialww@163.com (W.L.); yucao@wzu.edu.cn (Y.C.)

* Correspondence: Correspondence: chwxu@szu.edu.cn (C.X.); xw@wzu.edu.cn (W.X.); Tel.: +86-0755-26531501 (C.X.)

Received: 17 January 2019; Accepted: 14 February 2019; Published: 26 February 2019

Abstract: In this study, laser sintering of TiO₂ nanoparticle films on plastic substrates was conducted in order to improve the incident photon-to-electron conversion efficiency (IPCE) of flexible dye-sensitized solar cells (DSCs). Lasers with different wavelengths (355 nm and 1064 nm) were used to process the TiO₂ electrodes. With an optimized processing parameter combination, the 1064 nm laser can sinter 13 μm thick TiO₂ films uniformly, but the uniform sintering cannot be achieved by the 355nm ultraviolet (UV) laser, since the films possess a high absorption ratio at 355 nm. The experimental results demonstrate that the near-infrared laser sintering can enhance the electrical connection between TiO₂ nanoparticles without destroying the flexible plastic substrate, reduce the transmission impedance of electrons and increase the absorption rate of incident light. Furthermore, the charge collection efficiency, fill factor, and short-circuit current have all been improved to some extent, and the solar conversion efficiency increased from 4.6% to 5.7%, with an efficiency enhancement reaching 23.9%.

Keywords: 1064 nm laser; TiO₂ films; laser sintering; flexible dye-sensitized solar cells

1. Introduction

Dye-sensitized solar cells (DSCs) have become one of the substitutes for traditional silicon solar cells owing to the simple fabrication process and low fabrication cost [1–3]. The highest efficiency of DSC has reached ~13% [4,5], almost catching up with that of amorphous Si solar cells [6]. Moreover, DSCs can be fabricated on flexible substrates as a flexible solar cell [7,8], which has the advantages of easy transportation and roll-to-roll production [9,10]. However, the incident photon-to-electron conversion efficiency (IPCE) of flexible DSCs has been relatively low. For conventional DSCs prepared on conductive glass substrates, the heart is a several micrometer mesoporous TiO₂ layer, which needs to be annealed at 450–500 °C to remove the organic additive and achieve electrical connections between the nanoparticles [11,12]. The widely used indium tin oxide (ITO)-PET or ITO-PEN plastic substrates can only endure thermal treatment below 120 °C or 150 °C, which precludes any high-temperature sintering processes and the use of organic binders.

Until now, much efforts has been made to improve the inter-nanoparticle physical/electrical contacts of flexible DSCs with a low temperature, including compression [13–15], lift-off technique [16], ultraviolet (UV) irradiation [17,18], and chemical sintering [19,20]. However, a highly efficient and large-area fabrication technique for industrial production still remains a great challenge. Recently, numerous studies on laser processing of TiO₂ films have been conducted [21–23]. For example, a laser

assisted nano-particle deposition system was applied to successfully form sintered TiO₂ films on flexible substrates [24]. The deposition process with a feed rate of 0.025 mm/s is time-consuming, and the corresponding efficiency is only 1.92%. Meanwhile, UV and near-infrared fiber lasers were both used to generate mesoporous nano-crystalline TiO₂ films on ITO or fluorine-doped tin oxide (FTO) coated glasses with a sintering process [25–28]. However, the conductive glass substrates can withstand a much higher temperature than polyethylene naphthalate (PEN) and polyethylene terephthalate (PET) substrates, so the corresponding laser sintering technologies are not suitable for flexible DSCs. Shu Zhu et al. fabricated a flexible DSC via membrane transferring and laser sintering [29], and an efficiency of 4.65% could be achieved. Nevertheless, the TiO₂ nanotube membrane fabricated by a potentiostatic anodization method still needs to be annealed at 450 °C [30], and the detachment process of TiO₂ nanotube arrays is not suitable for industrial production. To simply sinter the TiO₂ nanoparticles films on plastic substrates, Ming et al. proposed to use selective laser sintering to improve the efficient of flexible DSCs [31], with a sintering efficiency of 0.02 m²/h, an ICPE of 5.6% could be achieved. Even so, the sintering efficiency struggles to meet the requirement of industrial production, and the corresponding improvement approach was not proposed. Besides, the key laser parameters determining the sintering effect were not systematically investigated, and the potential laser sintering mechanism was not demonstrated. These contents are of great significance for large-scale industrial production.

Laser sintering efficiency is very important for industrial manufacture, and the influence of sintering parameters on the photoelectric performance of flexible DSCs is of great significance to design the laser sintering system and improve the sintering efficiency. In this paper, to improve the IPCE of flexible DSCs, we reported a simple approach to sinter TiO₂ nanoparticle electrodes using a laser processing technique, which is a method of easy operation and fast fracture as well as industrialization continuous production. Two kinds of lasers with wavelengths of 355 nm and 1064 nm were used to sinter the TiO₂ electrodes, and the key parameters and characteristics of the laser sintering were presented. In addition, the effect of the laser wavelength on the laser sintering mechanism was systematically analyzed. The IPCE and the current-voltage (I–V) characteristic of the flexible DSC were also measured to determine the feasibility of the proposed technique.

2. Experimental Equipment, Materials and Methods

Typically, 3.0 g TiO₂ nanoparticles (Degussa, P25, Evonik, Essen, North Rhine-Westphalia, Germany) mixed with 7.0 g ethanol (Zhongrong Technology, Inc., Shanghai, China) were ball-milled at a speed of 350 rpm for 4 h to obtain a binder-free paste. Then, the paste was uniformly coated on an ITO-PEN substrate (14 Ω/cm², Peccell Technologies, Inc., Yokohama, Japan) by a doctor-blade technique. After being dried at 120 °C for 15 min in air, the films were compressed in a cold isostatic pressing (CIP) machine (Xinghualong, Inc., Suzhou, Jiangsu, China). The applied pressure was 200 MPa and the holding time was 300 s.

A schematic diagram of the equipment used for the laser sintering is shown in Figure 1a. A 355 nm Nd:YVO₄ laser (Inno Laser, Inc., Shenzhen, Guangdong, China) with the pulse width of 42 ns at 100 kHz was employed as the one laser source and the other laser source was a continuous wave (CW) fiber laser (IPG Photonics, Oxford, Mississippi, USA) with a wavelength of 1064 nm. Beam expanders were used to improve the laser beam quality. A 2D galvanometer scanner system was used to control the laser beam according to the designed pattern (Figure 1c). As an appropriate defocusing amount is beneficial for increasing the spot diameter and the uniformity of laser energy distribution on the film surface, and the sintering efficiency can also be improved by increasing the spot diameter, the focus of the laser beam was set above the TiO₂ film (Figure 1b).

After laser sintering, the TiO₂ films were soaked in a 0.5 mM N719 dye solution for 18 h. Then the dyed films were attached with a Pt|ITO|PEN counter electrode. Finally, the electrolyte, comprising 1.0 M 1,3-dimethylimidazolium iodide, 50 mM LiI, 30 mM I₂, 0.5 M tert-butylpyridine, and 0.1 M

guanidinium thiocyanate in a mixture of acetonitrile and valeronitrile (85:15, by volume) was injected into the cell.

The microstructure of TiO_2 films was analyzed by a field emission scanning electron microscope (FE-SEM, FEI-Sirion 200, FEI, Hillsboro, Oregon, USA). The thickness of TiO_2 films was measured by a surface profilometer (Veeco Dektak 150). Raman measurement was carried out using a WITec confocal Raman spectroscopy (alpha 300R, WITec, Ulm, Baden-Württemberg, Germany) with the spectral resolution of 1 cm^{-1} . A 532 nm laser (2.33 eV) with the power below 0.1 mW was used as the laser excitation, and the laser beam was focused using a $100\times$ objective lens ($\text{NA} = 0.95$). The photovoltaic performance of the cell was evaluated using a Keithley 2400 Source Meter (Keithley, Beaverton, Oregon, USA) under a light intensity of 100 mW/cm^2 at air mass (AM) 1.5G, the IPCE used for optimizing the laser sintering parameters was the maximum value achieved from the same ten specimens. A $4 \times 4\text{ mm}^2$ square mask was put on top of the device during the photovoltaic testing.

Figure 1. (a) Schematic device configuration and (b) sintering process, (c) scanning trace of the laser sintering, and (d) spectral absorption of different films. ITO: indium tin oxide; PEN: polyethylene naphthalate.

3. Experimental Results and Discussion

3.1. UV Laser Sintering

The TiO_2 nanoparticles used in this paper are rather transparent in the near-infrared (IR) region but are highly absorbent at UV wavelengths below 385 nm (Figure 1d), so a 355 nm UV laser is first chosen for the sintering with a scanning speed of 80 mm/s, a scanning interval of 5 μm , and a defocusing amount of 3.6 mm. Figure 2 shows the SEM images of the surface morphologies taken after sintering with different laser fluence. The unmodified TiO_2 film consists of tightly packed nanoparticles with a size of 30–40 nm (Figure 2b), and no obvious morphological change is observed when the laser fluence is below 0.28 J/cm^2 . As the laser fluence increases to 0.4 J/cm^2 , the TiO_2 nanoparticles agglomerate into irregular-shaped large ones (Figure 2d), which is analogous to the result achieved in high temperature ($800\text{ }^\circ\text{C}$) sintering [32]. This event provides evidence to support that the energy transfers from the laser to the TiO_2 film, which results in the enhanced bonding force between nanoparticles. However, the cross-sectional image shows that (Figure 2e), for the $\sim 13\mu\text{m}$ thickness film, the thickness of the melted layer is only about 250 nm. That is because the UV absorption of TiO_2 film is high to 98.5%,

which leads to that the weak scattering and reflection of the UV laser. Meanwhile, the decreased interspace in the sintered thin layer further limits the action depth of the UV laser.

Figure 2. Scanning electron microscope (SEM) images of (a) original TiO₂ film, ultraviolet (UV) laser sintered TiO₂ films with the laser fluence of (b) 0.22 J/cm², (c) 0.28 J/cm², and (d) 0.4 J/cm², (e) section image of laser sintered TiO₂ film with the laser fluence of 0.4 J/cm².

3.2. IR Laser Sintering

Since the spectral absorption of TiO₂ films at 1064 nm is much smaller than that at 355 nm, and the incident beam with a wavelength of 1064 nm can transmit through the films (Figure 1d), the whole film can be modified, so the 1064 nm fiber laser may be more suitable for sintering the TiO₂ films. The diameter of the laser spot is about 0.4 mm with a defocusing distance of 8 mm, and the scanning speed is fixed at 30 mm/s. Figure 3 shows the micrographs of the 1064 nm fiber laser sintered TiO₂ films. The main ingredients of the paste for preparing the TiO₂ films are absolute ethanol and TiO₂ nanoparticles, after the doctor-blade coating procedure, as the absolute ethanol volatilizes to air, the TiO₂ films shrink horizontally to form some microcracks (Figure 3a). When the laser power density is 4.5×10^3 W/cm², there is no obvious change on the film surface (Figure 3b). As the power density increases to 5.88×10^3 W/cm², the number of the microcracks is reduced (Figure 3c), but the size of the microcracks increases obviously, and the enlarged microcracks are arranged in parallel with each other. This indicates that the laser sintering promotes the further shrinking of the TiO₂ films. When the power density increases to 6.53×10^3 W/cm², the excessive heat transmitting to the PEN substrate will lead to a thermal deformation (Figure 3d), and one part of the TiO₂ nanoparticles break off from the flexible substrate.

The mechanical adhesion strength of the TiO₂ nanoparticle film can be measured by the ISO/DIS 15184 method [15,33], which determines the film hardness by scratching with a pencil. The non-sintered TiO₂ nanoparticle film is easily scratched with a 1B pencil. Also, the TiO₂ film sintered with a power density of 5.88×10^3 W/cm² cannot be scratched using a pencil with the hardness up to HB, which indicates that the IR laser sintering with a suitable laser power density can improve the connection between TiO₂ nanoparticles. However, the field emission SEM images show that the IR laser induced morphologic changes are not obvious (Figure 3e,f).

Figure 3. Microscope photographs of IR laser sintered TiO_2 films with the laser power density of (a) 0, (b) $4.5 \times 10^3 \text{ W/cm}^2$, (c) $5.88 \times 10^3 \text{ W/cm}^2$, (d) $6.53 \times 10^3 \text{ W/cm}^2$, SEM images of (e) original TiO_2 film, (f) IR laser sintered TiO_2 films with the laser power density of $5.88 \times 10^3 \text{ W/cm}^2$.

As the interspaces between nanoparticles are increased by the volatilization of absolute ethanol after doctor-blade coating procedure, the IPCE of the original sample is low (less than 0.7%), even if for the IR laser treated TiO_2 film, the IPCE is still less than 1%. The CIP procedure can effectively eliminate the increased interspace between TiO_2 nanoparticles; with this technology, the ICPE of the original sample is increased to 4.5%. For the laser sintering of TiO_2 nanoparticle films, power density is a key parameter, as shown in Figure 4a. With the increasing power density, the IPCE of flexible DSC increases linearly, and the maximum IPCE is achieved at the power density of $5.88 \times 10^3 \text{ W/cm}^2$. When the power density is further increased to $6.18 \times 10^3 \text{ W/cm}^2$, due to the thermal deformation of the flexible substrate, one part of the TiO_2 nanoparticles falls off, which results in a sharp decline in IPCE.

Figure 4. Effect of (a) laser power density and (b) scanning speed on the IPCE of the flexible DSCs based on laser sintered TiO₂ films.

For a continuous-wave laser, when the power density and scanning interval are fixed, the laser energy radiating to a unit area depends on the scanning speed, which can be expressed as the following equations:

$$\Phi = \frac{Pt}{d_0 V t} = \frac{P}{d_0 V} \quad (1)$$

where t is the time (s) of laser scanning, P is the laser power, d_0 is the spot diameter (μm), and V is the scanning speed. It can be seen that Φ is inversely proportional to the scanning speed. With a power density of $5.88 \times 10^3 \text{ W/cm}^2$, a spot diameter of 0.4 mm, and a scanning pitch of 0.25 mm, Figure 4b shows the effect of scanning speed on the IPCE of laser sintered flexible DSC. When the scanning speed is less than 20 mm/s, the energy accumulated by the low scanning speed is too high, so the IPCE of the laser sintered flexible DSC is even less than that of the original sample (4.5%). As the scanning speed increases, the IPCE increases. However, when the scanning speed is higher than 40 mm/s, the IPCE constantly decreases, and with a scanning speed of 60 mm/s, the IPCE of laser sintered flexible DSC is equal to that of the original sample. So in this paper, the optimal parameter combination for IR laser sintering is a power density of $5.88 \times 10^3 \text{ W/cm}^2$ and a scanning speed of 30 mm/s. As shown in Equation 1, by increasing the power density and scanning speed in equal proportions, Φ can be kept constant. Therefore, the laser sintering efficiency can be improved by increasing the scanning speed with a higher power density. Besides, with an optimal Φ , splitting the laser beam or shaping the point laser source into a line source can further improve the sintering efficiency.

To eliminate the accidental factors in the fabrication process of flexible DSCs, hundreds of flexible DSCs are prepared based on the laser sintered and unsintered TiO₂ films. The result (Figure 5a) shows that the IPCE of the IR treated DSCs is mainly concentrated in the range of 5.2%–5.7%, which is higher than that of the original sample (3.9–4.5%). As shown in Table 1, after the IR laser sintering, the maximal IPCE of the flexible DSCs is improved from 4.5% to 5.7%, the increase rate reaches 23.9%. Meanwhile, the short circuit current is increased from 9.2 mA/cm² to 10.4 mA/cm² (Figure 5b), and the fill factor is also significantly improved from 0.71 to 0.77. Those results reveal that the IR laser sintering plays a positive role in improving the performance of the flexible DSCs.

Table 1. Performance of the flexible dye-sensitized solar cells (DSCs) based on the laser sintered and unsintered TiO₂ films. IPCE: incident photon-to-electron conversion efficiency.

Samples	Voc (mV)	Jsc (mA/cm ²)	Fill Factor	IPCE
Original	720	9.2	0.71	4.6%
Laser sintered	716	10.4	0.77	5.7%

Figure 5. (a) Incident photon-to-electron conversion efficiency (IPCE) stability test, (b) current density-voltage, and (c) apparent recombination lifetime of the flexible dye-sensitized solar cells (DSCs) based on the laser sintered and unsintered TiO₂ films, (d) Raman spectra of the TiO₂ nanoparticle films before and after the laser sintering.

The photoelectric performance of DSCs depends mainly on two aspects, one is the absorption rate of the incident light, and the other is the collection efficiency of electrons. To improve the collection efficiency, the electrons which do not go through the external circuit and directly combine with the electrolyte should be inhibited as far as possible. The charge collection efficiency is determined by the dynamic competition between the internal electron transport and recombination [34]. The longer the electron lifetime is, the higher the charge collection efficiency is. Figure 5c shows the effect of incident light intensity on the apparent electron lifetime, and indicates that the IR laser sintering increases the electron lifetime between the TiO₂ conduction band and electrolyte redox potential, which results in an improvement of the charge collection efficiency.

To further study the effect of IR laser sintering on P25 TiO₂ nanoparticle films, the micro Raman spectroscopy technology is applied to detect and analyze the IR laser sintered TiO₂ nanoparticle films (Figure 5d). Since commercial P25 consists of about 80% anatase and 20% rutile TiO₂ phase [35], for the Raman spectrum of the original sample, the peaks, such as 144, 399, 519 (overlap with 515), and 639 cm⁻¹, represent anatase phase [36,37], and the Raman peaks belonging to the rutile phase (235 cm⁻¹, 445 cm⁻¹ and 612 cm⁻¹) are weak. However, after the IR laser sintering, the characteristic peaks of rutile are significantly enhanced, indicating that the proportion of rutile phase in the TiO₂ nanoparticle film is increased. This reveals that one part of the nanoparticles in the P25-type TiO₂ film is transformed from anatase phase to rutile phase by the laser sintering.

In the conventional high-temperature sintering process, to realize the transformation from anatase phase to rutile phase, TiO₂ nanoparticles are required to be heated above 550 °C for several hours, so the IR laser realizes the high-temperature sintering of TiO₂ films on low melting point flexible substrates. In the aspect of optical properties, the refractive index of rutile phase is higher than that of anatase phase [38], and rutile phase possesses a stronger scattering ability, it is widely used as a scattering layer in DSCs to increase the absorption rate of incident light [39,40]. Therefore, the IR

laser sintering not only increases the charge collection efficiency, but also enhances the absorption of incident light. These two factors ultimately result in the improved performance of the flexible DSCs.

3.3. Mechanism of the Laser Sintering

For the TiO_2 nanoparticles with 80% anatase and 20% rutile phase, since the band gaps of anatase and rutile phases are 3.2 eV and 3.0 eV [15,34], respectively, and the photon energy of 355 nm UV laser is 3.49 eV, the TiO_2 films can achieve a high absorption at the wavelength of 355 nm. As shown in Figure 6a, when the UV laser irradiates the TiO_2 film, the top layer of the TiO_2 film is sintered first, as the UV scattering of TiO_2 nanoparticles is weak, the heating applied to the lower layer nanoparticles only depends on the heat conduction from the top layer. According to the thermal diffusivity of nanostructured TiO_2 films ($0.3\text{--}0.5\text{ cm}^2/\text{s}$), when the UV laser sintering is conducted with the laser fluence of $0.4\text{ J}/\text{cm}^2$, during the duration of a single pulse (40 ns), the thickness of TiO_2 film heated to over 450°C by the heat conduction is only 54.6–70.6 nm [32]. If the laser influence further increases, the top layer TiO_2 nanoparticles are superheated and lose porosity. Therefore, the 355 nm UV laser cannot achieve uniform sintering for the $13\text{ }\mu\text{m}$ thick TiO_2 nanoparticle film.

Figure 6. Schematic diagrams of the laser sintering with the wavelength of (a) 355 nm and (b) 1064 nm.

The photon energy of IR laser (only 1.17 eV) is not only smaller than that of a 355 nm UV laser (3.49 eV), but also smaller than the band gaps of anatase phase (3.2 eV) and rutile phase (3.0 eV), which leads to the sintering mechanism of a IR laser being vastly different to that of a UV laser. TiO_2 is a weak n-type metal oxide semiconductor [41]. In general, there are some oxygen vacancy defects in the crystal lattices, which lead to the TiO_2 existing in the form of TiO_{2-x} , such as $\text{TiO}_{1.98}$ or $\text{TiO}_{1.95}$, x represents the extent of oxygen vacancy defects. The oxygen vacancy locates between the valence band and conduction band, which enables it to capture electrons with an energy of 0.76 eV. Therefore, the TiO_2 nanoparticles have a certain degree of absorption in the IR region, but the absorption is much smaller than that in the UV region.

When the TiO_2 nanoparticle film is sintered by the IR laser, as the laser absorptivity is low, and the size of nanoparticles is much smaller than the laser wavelength, only a fraction of laser energy is absorbed by the top-layer TiO_2 nanoparticles, most of the energy is scattered (Figure 6b). Meanwhile, the interspaces between the TiO_2 nanoparticles provide a channel for the propagation of scattered

light, so the IR laser can penetrate through the whole TiO₂ nanoparticle film, which results in the uniform sintering. Moreover, the continuous laser scattering inside the TiO₂ nanoparticle film leads to the multiple absorptions of laser energy by the TiO₂ nanoparticles. During the process of IR laser sintering, the entire nanoparticle layer reaches the phase transition temperature (about 550 °C) in a short time, and part of the nanoparticles are transformed from the anatase phase to the rutile phase, which leads to the enhancement of natural light scattering. Meanwhile, the absorption of incident light is also improved. During the process of phase transformation, “neck-type” connections are formed between the nanoparticles in the thickness direction of TiO₂ films, the enhanced electrification connection results in the improvement of electron collection efficiency, and the performance of the flexible DSC is promoted.

4. Conclusions

Flexible DSCs with TiO₂ nanoparticle films coated on plastic substrates are successfully improved by laser sintering. Though the TiO₂ films possess a high absorption rate at 355 nm wavelength, the uniform sintering for 13 µm thick TiO₂ cannot be achieved by the UV laser. However, with the optimized processing parameters, the whole TiO₂ film can be modified by the 1064 nm laser sintering. During this process, part of the TiO₂ nanoparticles is transformed from the anatase phase to the rutile phase, which enhances the scattering of incident light. The IR laser sintering not only increases the charge collection efficiency, but also enhances the absorption of incident light. These two factors ultimately result in the improved performance of the flexible DSCs. The short circuit current is increased from 9.2 mA/cm² to 10.4 mA/cm², the fill factor is also significantly improved from 0.71 to 0.77, and the flexible DSCs achieved an improved IPCE of 5.7%, the increase rate reached 23.9%. The laser sintering is highly promising for integration into the roll-to-roll production of flexible DSCs.

Author Contributions: H.Y. and C.X. conceived and designed the experiments; W.L. performed the experiments; Y.C. analyzed the data; D.F. and W.X. contributed reagents/materials/analysis tools; H.Y. wrote the paper.

Acknowledgments: This work is supported by the National Natural Science Foundation of China (U1609209, 51375348), the National Science Foundation of SZU (2017023), and Zhejiang Provincial Natural Science Funds (LR15E050003, LQ18F050006).

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

References

1. Meng, X.; Yu, C.; Zhang, X.; Huang, L.; Rager, M.; Hong, J.; Qiu, J.; Lin, Z. Active sites-enriched carbon matrix enables efficient triiodide reduction in dye-sensitized solar cells: An understanding of the active centers. *Nano Energy* **2018**, *54*, 138–147. [[CrossRef](#)]
2. Liu, Q.; Gao, N.; Liu, D.; Liu, J.; Li, Y. Structure and Photoelectrical Properties of Natural Photoactive Dyes for Solar Cells. *Appl. Sci.* **2018**, *8*, 1697. [[CrossRef](#)]
3. Peddapuram, A.; Cheema, H.; McNamara, L.E.; Zhang, Y.; Hammer, N.I.; Delcamp, J.H. Quinoxaline-Based Dual Donor, Dual Acceptor Organic Dyes for Dye-Sensitized Solar Cells. *Appl. Sci.* **2018**, *8*, 1421. [[CrossRef](#)]
4. Kakiage, K.; Aoyama, Y.; Yano, T.; Oya, K.; Kyomen, T.; Hanaya, M. Fabrication of a high-performance dye-sensitized solar cell with 12.8% conversion efficiency using organic silyl-anchor dyes. *Chem. Commun.* **2015**, *51*, 6315. [[CrossRef](#)] [[PubMed](#)]
5. Yu, Y.; Zheng, H.; Zhang, X.; Liang, X.; Yue, G.; Li, F.; Zhu, M.; Li, T.; Tian, J.; Yin, G. An efficient dye-sensitized solar cell with a promising material of Bi₄Ti₃O₁₂ nanofibers/graphene. *Electrochim. Acta* **2016**, *215*, 543–549. [[CrossRef](#)]
6. Yella, A.; Lee, H.W.; Tsao, H.N.; Yi, C.; Chandiran, A.K.; Nazeeruddin, M.K.; Diau, E.W.; Yeh, C.Y.; Zakeeruddin, S.M.; Gratzel, M. Porphyrin-sensitized solar cells with cobalt (II/III)-based redox electrolyte exceed 12 percent efficiency. *Science* **2011**, *334*, 629–634. [[CrossRef](#)] [[PubMed](#)]
7. Peiris, T.A.N.; Senthilarasu, S.; Wijayantha, K.G.U. Enhanced Performance of Flexible Dye-Sensitized Solar Cells: Electrodeposition of Mg(OH)₂ on a Nanocrystalline TiO₂ Electrode. *J. Phys. Chem. C* **2012**, *116*, 1211–1218. [[CrossRef](#)]

8. Yoo, K.; Kim, J.; Lee, J.A.; Kim, J.; Lee, D.; Kim, K.; Kim, J.; Kim, B.; Kim, H.; Kim, W.M. Completely Transparent Conducting Oxide-Free and Flexible Dye-Sensitized Solar Cells Fabricated on Plastic Substrates. *ACS Nano* **2015**, *9*, 3760–3771. [[CrossRef](#)] [[PubMed](#)]
9. Senthilarasu, S.; Peiris, T.A.N.; García-Cañadas, J.; Wijayantha, K.G.U. Preparation of Nanocrystalline TiO₂ Electrodes for Flexible Dye-Sensitized Solar Cells: Influence of Mechanical Compression. *J. Phys. Chem. C* **2012**, *116*, 19053–19061. [[CrossRef](#)]
10. Lee, H.; Hwang, D.; Jo, S.M.; Kim, D.; Seo, Y.; Kim, D.Y. Low-Temperature Fabrication of TiO₂(2) Electrodes for Flexible Dye-Sensitized Solar Cells Using an Electrospray Process. *ACS Appl. Mater. Interfaces* **2012**. [[CrossRef](#)]
11. O'Regan, B.; Gratzel, M. A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **1991**, *353*, 737–740. [[CrossRef](#)]
12. Kim, H.-S.; Chun, M.-H.; Suh, J.S.; Jun, B.-H.; Rho, W.-Y. Dual Functionalized Freestanding TiO₂ Nanotube Arrays Coated with Ag Nanoparticles and Carbon Materials for Dye-Sensitized Solar Cells. *Appl. Sci.* **2017**, *7*, 576. [[CrossRef](#)]
13. Boschloo, G.; Lindström, H.; Magnusson, E.; Holmberg, A.; Hagfeldt, A. Optimization of dye-sensitized solar cells prepared by compression method. *J. Photochem. Photobiol. A* **2002**, *148*, 11–15. [[CrossRef](#)]
14. Weerasinghe, H.C.; Sirimanne, P.M.; Simon, G.P.; Cheng, Y.-B. Cold isostatic pressing technique for producing highly efficient flexible dye-sensitized solar cells on plastic substrates. *Prog. Photovolt. Res. Appl.* **2012**, *20*, 321–332. [[CrossRef](#)]
15. Yamaguchi, T.; Tobe, N.; Matsumoto, D.; Nagai, T.; Arakawa, H. Highly efficient plastic-substrate dye-sensitized solar cells with validated conversion efficiency of 7.6%. *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 812–816. [[CrossRef](#)]
16. Dürr, M.; Schmid, A.; Obermaier, M.; Rosselli, S.; Yasuda, A.; Nelles, G. Low-temperature fabrication of dye-sensitized solar cells by transfer of composite porous layers. *Nat. Mater.* **2005**, *4*, 607–611. [[CrossRef](#)] [[PubMed](#)]
17. Gutiérrez-Tauste, D.; Zumeta, I.; Vigil, E.; Domènech, X.; Ayllón, J.A. New low-temperature preparation method of the TiO₂ porous photoelectrode for dye-sensitized solar cells using UV irradiation. *J. Photochem. Photobiol. A Chem.* **2005**, *175*, 165–171. [[CrossRef](#)]
18. Lewis, L.N.; Spivack, J.L.; Gasaway, S.; Williams, E.D.; Gui, J.Y.; Manivannan, V.; Siclován, O.P. A novel UV-mediated low-temperature sintering of TiO₂ for dye-sensitized solar cells. *Sol. Energy Mater. Sol. Cells* **2006**, *90*, 1041–1051. [[CrossRef](#)]
19. Park, N.G.; Kim, K.M.; Kang, M.G.; Ryu, K.S.; Chang, S.H.; Shin, Y.J. Chemical Sintering of Nanoparticles: A Methodology for Low-Temperature Fabrication of Dye-Sensitized TiO₂ Films. *Adv. Mater.* **2005**, *17*, 2349–2353. [[CrossRef](#)]
20. Chen, W.; Qiu, Y.; Yang, S. A new ZnO nanotetrapods/SnO₂ nanoparticles composite photoanode for high efficiency flexible dye-sensitized solar cells. *Phys. Chem. Chem. Phys. PCCP* **2010**, *12*, 9494–9501. [[CrossRef](#)] [[PubMed](#)]
21. Mincuzzi, G.; Palma, A.L.; Di Carlo, A.; Brown, T.M. Laser Processing in the Manufacture of Dye-Sensitized and Perovskite Solar Cell Technologies. *ChemElectroChem* **2016**, *3*, 9–30. [[CrossRef](#)]
22. Mincuzzi, G.; Vesce, L.; Schulz-Ruhtenberg, M.; Gehlen, E.; Reale, A.; Di Carlo, A.; Brown, T.M. Taking Temperature Processing Out of Dye-Sensitized Solar Cell Fabrication: Fully Laser-Manufactured Devices. *Adv. Energy Mater.* **2014**, *4*, 1400421. [[CrossRef](#)]
23. Lu, B.; Lan, H.; Liu, H. Additive manufacturing frontier: 3D printing electronics. *Opto-Electron. Adv.* **2018**, *1*, 170004. [[CrossRef](#)]
24. Lee, J.; Choi, J.O.; Jeong, J.; Yang, S.; Ahn, S.; Kwon, K.; Lee, C.S. Energy harvesting of flexible and translucent dye-sensitized solar cell fabricated by laser assisted nano particle deposition system. *Electrochim. Acta* **2013**, *103*, 252–258. [[CrossRef](#)]
25. Mincuzzi, G.; Vesce, L.; Liberatore, M.; Reale, A.; Di Carlo, A.; Brown, T.M. Laser-sintered TiO₂ films for dye solar cell fabrication: An electrical, morphological, and electron lifetime investigation. *IEEE Trans. Electron Devices* **2011**, *58*, 3179–3188. [[CrossRef](#)]
26. Malyukov, S.; Sayenko, A. Laser sintering of a porous TiO₂ film in dye-sensitized solar cells. *J. Russ. Laser Res.* **2013**, *34*, 531–536. [[CrossRef](#)]

27. Mincuzzi, G.; Schulz-Ruhtenberg, M.; Vesce, L.; Reale, A.; Di Carlo, A.; Gillner, A.; Brown, T.M. Laser processing of TiO₂ films for dye solar cells: A thermal, sintering, throughput and embodied energy investigation. *Prog. Photovolt. Res. Appl.* **2014**, *22*, 308–317. [[CrossRef](#)]
28. Hadi, A.; Alhabrardi, M.; Chen, Q.; Liu, H.; Guo, W.; Curioni, M.; Cernik, R.; Liu, Z. Rapid fabrication of mesoporous TiO₂ thin films by pulsed fibre laser for dye sensitized solar cells. *Appl. Surf. Sci.* **2018**, *428*, 1089–1097. [[CrossRef](#)]
29. Lin, J.; Zhu, S.; Chen, X.; Liu, X. Low temperature transferring of anodized TiO₂ nanotube-array onto a flexible substrate for dye-sensitized solar cells. *Opt. Mater. Express* **2015**, *5*, 2754.
30. Lin, J.; Chen, J.; Chen, X. High-efficiency dye-sensitized solar cells based on robust and both-end-open TiO₂ nanotube membranes. *Nanoscale Res. Lett.* **2011**, *6*, 475. [[CrossRef](#)] [[PubMed](#)]
31. Ming, L.; Yang, H.; Zhang, W.; Zeng, X.; Xiong, D.; Xu, Z.; Wang, H.; Chen, W.; Xu, X.; Wang, M.; et al. Selective laser sintering of TiO₂ nanoparticle film on plastic conductive substrate for highly efficient flexible dye-sensitized solar cell application. *J. Mater. Chem. A* **2014**, *2*, 4566. [[CrossRef](#)]
32. Kim, J.; Lee, M. Laser welding of nanoparticulate TiO₂ and transparent conducting oxide electrodes for highly efficient dye-sensitized solar cell. *Nanotechnology* **2010**, *21*, 345203. [[CrossRef](#)] [[PubMed](#)]
33. Shao, J.; Liu, F.; Dong, W.; Tao, R.; Deng, Z.; Fang, X.; Dai, S. Low temperature preparation of TiO₂ films by cold isostatic pressing for flexible dye-sensitized solar cells. *Mater. Lett.* **2012**, *68*, 493–496. [[CrossRef](#)]
34. Bisquert, J.; Zaban, A.; Salvador, P. Analysis of the mechanisms of electron recombination in nanoporous TiO₂ dye-sensitized solar cells. Nonequilibrium steady-state statistics and interfacial electron transfer via surface states. *J. Phys. Chem. B* **2002**, *106*, 8774–8782. [[CrossRef](#)]
35. Yan, M.; Chen, F.; Zhang, J.; Anpo, M. Preparation of controllable crystalline titania and study on the photocatalytic properties. *J. Phys. Chem. B* **2005**, *109*, 8673–8678. [[CrossRef](#)] [[PubMed](#)]
36. Zhang, J.; Li, M.; Feng, Z.; Chen, J.; Li, C. UV Raman spectroscopic study on TiO₂. I. Phase transformation at the surface and in the bulk. *J. Phys. Chem. B* **2006**, *110*, 927–935. [[CrossRef](#)] [[PubMed](#)]
37. Swamy, V.; Kuznetsov, A.; Dubrovinsky, L.S.; Caruso, R.A.; Shchukin, D.G.; Muddle, B.C. Finite-size and pressure effects on the Raman spectrum of nanocrystalline anatase TiO₂. *Phys. Rev. B* **2005**, *71*, 184302. [[CrossRef](#)]
38. Gao, Q.; Wu, X.; Fan, Y.; Zhou, X. Low temperature synthesis and characterization of rutile TiO₂-coated mica–titania pigments. *Dyes Pigm.* **2012**, *95*, 534–539. [[CrossRef](#)]
39. Lan, Z.; Wu, J.-H.; Lin, J.-M.; Huang, M.-L. Synthesis of rutile TiO₂ nanorod and application in dye-sensitized solar cell. *J. Inorg. Mater.* **2011**, *2*, 003.
40. Wang, H.; Miyauchi, M.; Ishikawa, Y.; Pyatenko, A.; Koshizaki, N.; Li, Y.; Li, L.; Li, X.; Bando, Y.; Golberg, D. Single-crystalline rutile TiO₂ hollow spheres: Room-temperature synthesis, tailored visible-light-extinction, and effective scattering layer for quantum dot-sensitized solar cells. *J. Am. Chem. Soc.* **2011**, *133*, 19102–19109. [[CrossRef](#)] [[PubMed](#)]
41. Nakano, Y.; Morikawa, T.; Ohwaki, T.; Taga, Y. Origin of visible-light sensitivity in N-doped TiO₂ films. *Chem. Phys.* **2007**, *339*, 20–26. [[CrossRef](#)]