

Article

Localized Surface Plasmon-Enhanced Infrared-to-Visible Upconversion Devices Induced by Ag Nanoparticles

Yuyi Zhang ¹, Chengjun Liu ¹, Xingyu Liu ¹, Ziyu Wei ¹, Hui Tao ¹, Feng Xu ¹, Lixi Wang ², Jiangyong Pan ², Wei Lei ^{1,*} and Jing Chen ^{1,*}

¹ Joint International Research Laboratory of Information Display and Visualization, School of Electronic Science and Engineering, Southeast University, Nanjing 210018, China

² School of Electronic and Information Engineering, Nanjing University of Information Science & Technology, Nanjing 210044, China

* Correspondence: lw@seu.edu.cn (W.L.); chenjing@seu.edu.cn (J.C.)

Abstract: Upconversion devices (UCDs) have motivated tremendous research interest with their excellent potential and promising application in photovoltaic sensors, semiconductor wafer detection, biomedicine, and light conversion devices, especially near-infrared-(NIR)-to-visible upconversion devices. In this research, a UCD that directly turned NIR light located at 1050 nm into visible light located at 530 nm was fabricated to investigate the underlying working mechanism of UCDs. The simulation and experimental results of this research proved the existence of the quantum tunneling phenomenon in UCDs and found that the quantum tunneling effect can be enhanced by a localized surface plasmon.

Keywords: upconversion device; quantum tunneling; localized surface plasmon (LSP)



Citation: Zhang, Y.; Liu, C.; Liu, X.; Wei, Z.; Tao, H.; Xu, F.; Wang, L.; Pan, J.; Lei, W.; Chen, J. Localized Surface Plasmon-Enhanced Infrared-to-Visible Upconversion Devices Induced by Ag Nanoparticles. *Materials* **2023**, *16*, 1973. <https://doi.org/10.3390/ma16051973>

Academic Editor: Antonio Polimeni

Received: 29 January 2023

Revised: 23 February 2023

Accepted: 26 February 2023

Published: 28 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Numerous research studies on upconversion devices (UCDs) have been reported, owing to their application in photovoltaic sensors, semiconductor wafer detection, biomedicine, and light conversion devices, especially devices that can turn near-infrared (NIR) light to visible light [1–5]. Early NIR UCDs were integrated with infrared photodetectors and visible light emitters, which involve complicated steps [6–8]. This is because the InGaAs detector and the Si-based readout circuit grow on different substrate materials, which need to be prepared separately, and then need to be connected one-to-one through an indium column. However, since such NIR UCDs have some disadvantages, such as lattice mismatch (which can occur between the materials comprising the detector and the materials comprising light emitting diode) and the inability to prepare an NIR UCD in a large area (owing to the high costs of epitaxial grown inorganic devices) [9], other design structures of NIR UCDs have been considered [9,10]. The appearance of devices that could directly convert NIR light to visible light have greatly expanded the application of NIR UCDs. These types of devices have the advantages of fast response, simple structure, and convenient preparation [11]. Ban et al. first raised the concept in 2007 of integrating InGaAs/InP photodetectors and organic light-emitting diodes (OLEDs) directly into a new device [12]. Kim et al. have improved this device by changing the materials of each layer [2]. Unfortunately, there were too many layers in this new device structure, which made it impossible to complete carrier transfer efficiently. Many reports have indicated that metal nanoparticles could be helpful in carrier transport; thus, adding metal nanoparticles such as silver (Ag) is of great significance for the improvement of UCDs [13,14]. Consequently, Zhou et al. prepared similar devices in 2020, which marked great progress in UCDs [10].

The addition of Ag nanoparticles (NPs) is particularly important for the upconversion of NIR light while studying these devices. Metal nanoparticles have a great influence in the quantum domain due to their size, such as the quantum size effect and quantum

tunneling effect. The unique properties of metal nanoparticles ensure they have promising applications in optical, electrical, biological, and chemical catalysis [15–17]. Previous experiments have also found that Ag NPs feature good optical and electrical properties [18], such as enhancement of Raman spectra by Ag nanoparticles [19] and increased device conductivity owing to the good carrier transport characteristics of Ag [20]. This paper will focus on a more noteworthy property, the localized surface plasmon effect produced by Ag NPs, which greatly improves the performance of UCDs [13,14]. Moreover, relevant studies have shown that gold (Au) nanoparticles can generate hot hole-electron pairs under illumination [21]. Therefore, the existence of Ag NPs should also produce hole-electron pairs, which to some extent increases the current density and electric field strength, making quantum tunneling more obvious [22]. Because of these excellent properties, various devices containing Ag NPs have developed rapidly. In 2020, an array of Ag NPs were designed which created Localized Surface Plasmon Resonance (LSPR) near the surface of silicon (Si) [14]. In another study, Yang et al. found that the lifetime was extended when the surface plasmon resonant peak of silver nanoparticles was adjusted to resonate with the Q- absorption band [23].

In the current research, a device structure that can turn NIR light located at 1050 nm into visible light located at 530 nm was fabricated to explain the tunneling mechanism in UCDs, which is similar to a switch sensitive to infrared light. The localized surface plasmon formed by the effective deposition of Ag NPs has proved to be possible through theoretical calculation, such that it can enhance the quantum tunneling effect in UCDs. The device characterization results verified the tunneling effect caused by Ag NPs under NIR light. In previously reported devices, excitons were recombined by holes generated in the photosensitive layer. After adding Ag NPs, holes could be injected from the ITO electrode, which greatly improved the performance of the device. The current research is significant in improving the performance of similar devices by understanding the working mechanism of UCDs. It may have a far-reaching impact on the preparation of optoelectronic devices.

2. Materials and Methods

Materials: Magnesium acetate tetrahydrate (Sigma-Aldrich, St. Louis, MO, USA, 99.99%), Zinc acetate dihydrate (Sigma-Aldrich, 99.99%), Tetramethyl ammonium Hydroxide (Sigma-Aldrich, >97%), Ethanol ($H_2O \leq 50$ ppm (by K.F.)), Meryer, Shanghai, China, 99.5%), Methyl sulfoxide ($H_2O \leq 50$ ppm (by K.F.)), Meryer, 99.7%), Silver nitrate (Sigma, 99.99%), Oleylamine (Aladdin, 80–90%), Toluene (Sinopharm, Beijing, China, >99.5%), Lead monoxide (Aladdin, 99.999%), Oleic acid (Adamas, >90%), 1-Octadecene (Macklin, >95%), Acetone (Sinopharm, >95%), Hexamethyldisilathiane (Energy chemical, 98%), Tetrabutyl ammonium iodide (Maya, >99%), Methanol (Acros, 99.9%), 1,2-Ethanedithiol (Sigma-Aldrich, >99%), Acetonitrile (Sigma-Aldrich, 99.8%), Molybdenyl acetylacetonate (Adamas, 99%), Poly [4,4'-(N-(4-secbutylphenyl)diphenylamine)] (p-OLED, MW > 40,000), CdSe/ZnS quantum dots (Mesolight), Nafion (Sigma-Aldrich), Isopropanol (Sinopharm, >99.7%)

About manufacturer and country from where the equipment was sourced, they are shown in Table S1 in supporting information.

Synthesis of $Zn_{0.95}Mg_{0.05}O$: We dissolved 0.1 mol of tetramethyl ammonium hydroxide (TMAH) in ultra-dry ethanol, 0.02 mol of zinc acetate and 0.00105 mol of magnesium acetate in dimethyl sulfoxide (DMSO), and mixed the two solutions vigorously for 1 h at room temperature to synthesize $Zn_{0.95}Mg_{0.05}O$ nanoparticles. The suspension was washed 3 times with absolute ethanol/acetone (1:3 volume ratio). Finally, the nanoparticles were dispersed in ultra-dry ethanol, about 30 mg/mL. (The suspension was centrifuged at 4000 r.p.m. for 5 min.)

Synthesis of PbS Quantum Dots(QDs): We dissolved 0.9 g (4.04 mmol) of lead oxide in 9 mL of mixed solvent consisting of oleic acid (OA)(3 mL) and 1-Octadecene (ODE) (6 mL). Then the mixed solution was heated under N_2 flow at 95 °C for 4 h, after which an additional 10 mL of ODE was added for further dilution. After that, 420 μ L of hexamethyldisilathiane (TMS) was dissolved in another 10 mL of ODE. The 10.42 mL of TMS solution was then

injected into the reaction solution at 122 °C, accompanied by vigorous stirring. We removed the heating jacket immediately after 30 s and used an ice water bath to cool down the mixed solution. Finally, while keeping the temperature of the solution at 20 °C, we isolated the nanocrystals by adding acetone. The obtained solid was dispersed in 12 mL of toluene for purification, and was precipitated again with acetone/hexane (1:4 volume ratio). The step above was repeated three times. Then it was precipitated once with acetone/octane (1:5 volume ratio), and finally dispersed in octane. (The suspension was centrifuged at 8500 r.p.m. for 5 min.) X-ray diffraction (XRD) spectra for structural analysis are shown in Figure S1.

Synthesis of Ag NPs: We dissolved 0.1359 g of AgNO₃ (0.8 mmol) in 3.2 mL of OLA and then add the mixed solution above into 80 mL of toluene. The solution was heated to 110 °C under a N₂ flow for 6 h, accompanied by vigorous stirring. After the reaction, the heating jacket was removed and the solution was cooled to room temperature by ice water bath. Finally, the Ag NPs were isolated by adding anhydrous ethanol. The obtained solid was washed with toluene/ethanol (1:4 volume ratio) twice, and then dissolved in toluene [10]. (The suspension was centrifuged at 6000 r.p.m. for 5 min.) XRD spectra for structural analysis are shown in Figure S2.

Synthesis of MoO_x Precursor: In the glove box filled with nitrogen, 20 mg of Molybdenyl acetylacetonate (MoO₂(acac)₂) was dissolved in a mixed solvent (1 mL) consisting of isopropanol and 1-butanol (1:1 volume ratio). The mixed solution was stirred on a hot plate at 60 °C for 1 h. Nafion was also diluted with a mixture of isopropanol and 1-butanol (1:1 volume ratio) to obtain a concentration of 5 wt%. Before spin coating, we stirred the two mixed solutions above for 20 min and dilute them 50 times. The final standard concentration of MoO₂(acac)₂ was 0.4 mg/mL, and the standard concentration of Nafion was kept at 0.1 wt% [24].

Simulated Software: Computer simulation technology (CST)

Device Fabrication: The structure of UCD was ITO/Zn_{0.95}Mg_{0.05}O/Ag NPs/PbS QDs/MoO_x/poly-TPD/(CdSe/ZnS) QDs/Zn_{0.95}Mg_{0.05}O/Ag electrode. ITO glass was cleaned using deionized water, acetone and isopropyl alcohol in that order in an ultrasonic bath for 10 min each, followed by ultraviolet treatment for 30 min. The substrates were then transferred to an N₂-filled glove box. In this environment, Zn_{0.95}Mg_{0.05}O nanoparticles were spin-coated on top of the pretreated ITO glass at 3000 r.p.m. for 30 s, followed by heat treatment at 70 °C for 10 min. Ag NPs (5 mg/mL) dissolved in octane were spin-coated on the Zn_{0.95}Mg_{0.05}O layer at 3000 r.p.m. for 30 s, followed by heat treatment at 70 °C for 5 min. Then, the PbS layer was deposited via layer-by-layer spin coating. For each layer, 400 µL of PbS solution were spin-cast onto the Zn_{0.95}Mg_{0.05}O substrate at 2000 r.p.m. for 15 s. A tetrabutylammonium iodide solution was then dropped onto the film and left for 30 s, followed by two rinse-spin steps using methanol. After that, a MoO_x precursor was spin-coated at 3000 r.p.m. and annealed at 70 °C for 15 min, and an electron-blocking layer was spin-coated onto the MoO_x substrate at 4000 r.p.m. for 60 s using poly-TPD solution, followed by heat treatment at 80 °C for 10 min. Then CdSe/ZnS QDs dissolved in octane was spin-coated at 2000 r.p.m. for 30 s, followed by heat treatment at 80 °C for 10 min. Afterwards the Zn_{0.95}Mg_{0.05}O film was spin coated at 2000 r.p.m. for 30 s, followed by heat treatment at 80 °C for 10 min. Finally, 120 nm Ag was deposited.

Characterizations: The absorption spectra were measured using a UV-Visible instrument (U-4100). The photoluminescence (PL) spectra were measured using an NIR spectrometer (Maya2000). The current-voltage-luminance (I-V-L) and current density-external quantum efficiency-luminance (J-EQE-L) characteristics were characterized using a Photo Research (PR670) spectrometer equipped with a source meter (Keithley 2400). The chemical compositions and film morphology were analyzed with an energy-dispersive spectrometer (EDS)-equipped field-emission scanning electron microscope (JEOL-7800F).

3. Results and Discussion

Firstly, the prepared quantum dot material was characterized to confirm whether it could meet the requirements of the further device preparation. Figure 1a shows the absorption spectra of PbS QDs located at 1050 nm and Figure 1b shows that the photoluminescence peak of the prepared PbS QDs was 1130 nm with NIR emission. Figure 1c shows the absorption spectra of CdSe/ZnS QDs located at 515 nm and Figure 1d shows that the photoluminescence peak of the prepared CdSe/ZnS QDs was 530 nm with green emission. The UCD mentioned above absorbed NIR light (~ 1050 nm) and emit green light (~ 530 nm). Then, the UCD was further prepared based on the two types of QD, i.e., PbS and CdSe/ZnS, and demonstrated that it could turn NIR light into visible light. (Excitation for Figure 1b was infrared light located at 1000 nm whose Peak Width at Half Height was 100 nm. Excitation for Figure 1d was visible light located at 525 nm.)

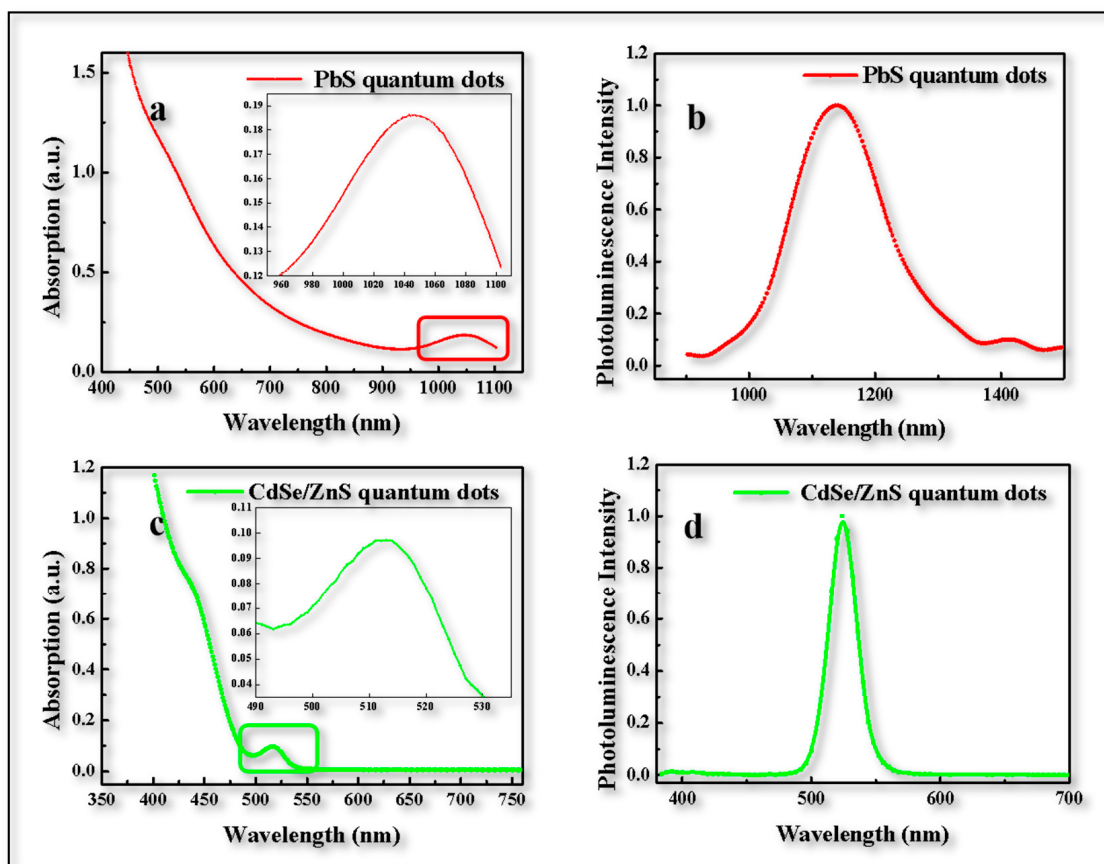


Figure 1. Quantum dot characterization. (a) Absorption spectra of PbS QD film, inset is detail view of peak position. (b) PL spectra of PbS QDs film. (c) Absorption spectra of CdSe/ZnS QDs film, inset is a detailed view of the peak position. (d) PL spectra of CdSe/ZnS QDs film.

The SEM and EDS results of $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ film modified by the Ag NP layer showed that the elements of Zn, O, and Ag were distributed uniformly (Figure 2), revealing the uniform composition of the film. Furthermore, it was found that there were some small islands of Ag NPs deposited on the surface of $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$, as shown in Figure 2.

Our second aim was to understand the mechanism of this UCD. In Figure 3a, the layers distributed between the ITO electrode and evaporation electrode Ag can be seen. From the bottom to the top, the device structure is illustrated as ITO (190 nm)/ $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ (100 nm)/Ag NPs (20 nm)/PbS QDs (400 nm)/ MoO_x (15 nm)/poly-TPD (15 nm)/(CdSe/ZnS) QDs (60 nm)/ $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ (80 nm)/Ag electrode (120 nm). The light-emitting area of this UCD was 4 mm^2 .

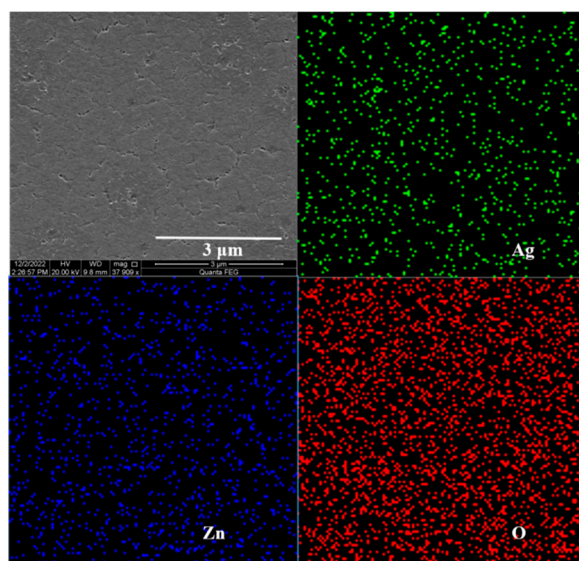


Figure 2. SEM characterization and EDS mapping of $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ films modified by Ag NPs.

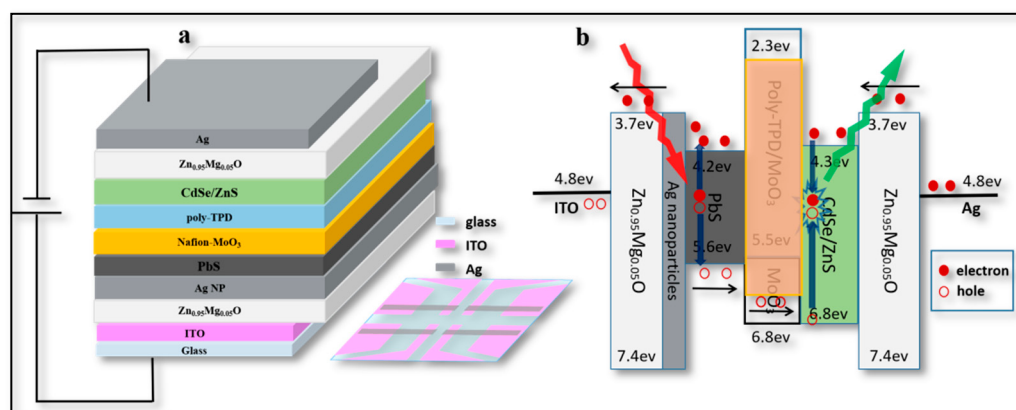


Figure 3. Structure of UCD. (a) Schematic cross-sectional view of UCD structure, inset is a top view of the device structure. (b) Energy level diagram of each film and carrier transfer mechanism.

To understand the working mechanism of the UCD, it was necessary to analyze the energy level relationship and carrier transfer process among the layers. As shown in Figure 3b, the highest occupied molecular orbital (HOMO) energy levels of $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$, PbS, poly-TPD, and CdSe/ZnS were 7.4 eV, 5.6 eV, 5.5 eV, and 6.8 eV, respectively. The lowest unoccupied molecular orbital (LUMO) energy levels of $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$, PbS, poly-TPD, and CdSe/ZnS were 3.7 eV, 4.2 eV, 2.3 eV, and 4.3 eV, respectively. The matched energy level of each layer ensured the efficient transfer of carriers in the device [25]. For one part, when PbS film was irradiated by NIR light (1050 nm), hole-electron pairs were generated and then moved under the horizontal electric field. Electrons were passed through the barrier between PbS and $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$, leaving holes to transfer from poly-TPD to CdSe/ZnS QDs. Meanwhile, some holes were injected from the ITO electrode and accumulated at the interface between ITO and $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ layer. For the other part, electrons were injected from the Ag electrode to CdSe/ZnS QDs through the $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ layer, thus electrons and holes could be combined within CdSe/ZnS QDs as excitons to emit light. Therefore, this type of UCD worked as a function to transfer NIR light (1050 nm) to green light (530 nm) in this work.

However, it was noticed that the HOMO level of $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ (~7.4 eV) was very far from that of ITO (~4.8 eV). The high valence band (VB) of $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ prevents holes from migrating at the interface of $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ and ITO, making it difficult for the device to light up [25]. The UCD could only work when the electrons generated from PbS QDs

passed through the barrier (~ 0.5 eV) between PbS and ITO under NIR light; meanwhile the holes generated from PbS QDs were transferred and recombined with electrons injected from the Ag electrode within CdSe/ZnS QDs. This was the key point of this type of UCD: to elucidate the function and switch the device on/off with or without NIR radiation.

Thus, in order to achieve the switching property, the function of $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}/\text{Ag}$ NPs could be further studied and the layers of this key part could be analyzed separately. If it was without NIR light, as in Figure 4a, the energy barrier between ITO and $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ would be high (~ 2.6 eV) with a thicker band bend; thus, holes could not easily cross through the barrier. When the NIR light was applied ($2 \text{ mw}/\text{cm}^2$), the band bend could be slightly increased [10], and the NIR light would result in pairs of electron holes in the PbS layer. If a positive bias was applied ($2\sim 4$ V), electrons could be moved and collected at the boundary between the $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ and PbS layers, and then pass through the barrier (~ 0.5 eV), as shown in Figure 4b [9]. In this case, the leaving holes generated within the PbS QDs could be transferred from poly-TPD to CdSe/ZnS QDs, combining with the electrons injected from the Ag electrode [26]. Thus, the upconversion process that switches the NIR light to green emission could be elucidated. However, a strong NIR source power would be necessary to generate more hole-electron pairs of carriers within PbS QDs [9]. In other words, NIR light with low intensity could not make the device work perfectly.

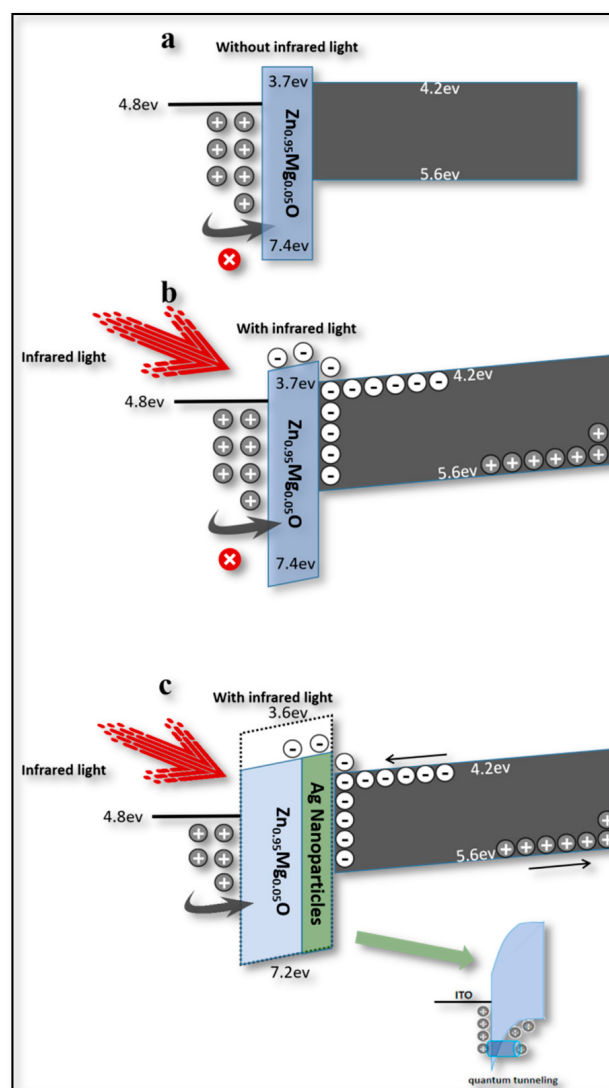


Figure 4. Potential barrier mechanism diagram of $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ and PbS interface. (a) Without Ag NPs and NIR light. (b) Without Ag NPs and with NIR light. (c) With Ag NPs and NIR light.

The VB of $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ [27] could be significantly bent with the addition of the Ag NP layer, increasing the chance for the holes accumulating and tunneling through the energy barrier at the interface between $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ and ITO [28]. In this way, more holes could participate in the formation of excitons, as a result of improving the brightness of the device and reducing the threshold voltage.

Next, in order to investigate the function of the Ag NPs layer in the upconversion process and its feasibility, a model was established to simulate the role of Ag NPs in this process by computer simulation technology (CST). This model was established on the basis of observing the morphology of Ag nanoparticles using a transmission electron microscope (TEM) (shown in Figure S3) which monitored the change of electric field on the film surface after applying near-infrared light. Ag NP islands were randomly generated at different positions in this model to ensure the credibility of the simulation model relative to the real nanoparticles. Through the established model, it was easily found that a force in the form of a localized surface plasmon (LSP) strengthened the electric field between $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ film when there was 1050 nm NIR light shining from below, and thus the tunneling was strengthened. The thickness of the $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ model was set to 100 nm and the radius of the square-like islands (Ag NPs) above the $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ film was 25 nm (see Figure 5a). From the simulation results, the obvious enhancement of the electric field near the Ag NPs islands can be seen (Figure 5b,c), which was consistent with the results of other different devices [29].

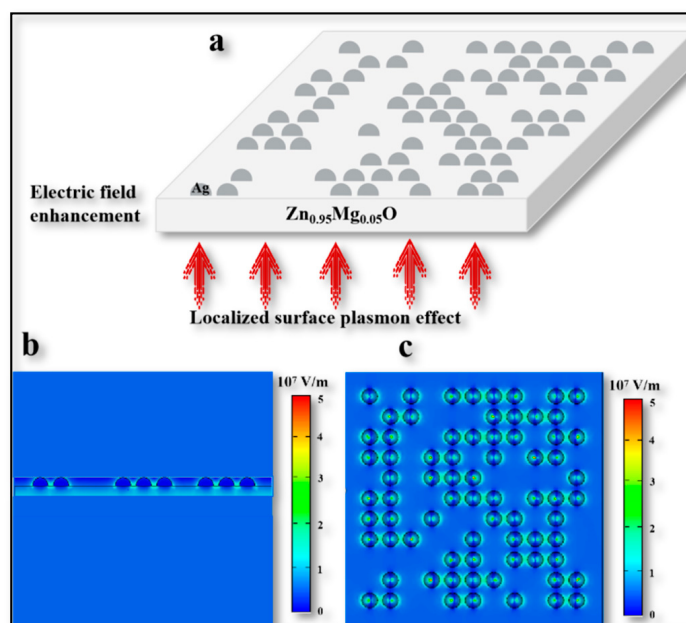


Figure 5. CST Simulation diagram. (a) Schematic diagram of established simulation model. (b) Section diagram of simulation results. (c) Vertical view of simulation results.

After the aforementioned process, the devices mentioned above were prepared in order to further demonstrate the role of Ag NPs. The upconversion devices were simply characterized and it was found that the performance of the device differed greatly with or without infrared light. Under NIR light, the brightness and external quantum efficiency (EQE) of the device were significantly improved, increasing about five times, as shown in Figure 6a,b. On the one hand, the reason for this could be that the photogenerated holes excited by infrared light within the PbS QDs layer were recombined with electrons injected from the cathode. On the other hand, as mentioned above, the enhanced quantum tunneling effect arising from the localized surface plasmon with the addition of Ag NPs were helpful in improving electroluminescence performance. In past research, the current of UCD without Ag NPs could only reach 10 A/m^2 [2], but in this research, it reached

2500 A/m² at a voltage of 4 V with a testing area of 4 mm², as shown in Figure 6c. To some extent, it was caused by the different materials of the NIR-sensitizing layer, which was SnPc:C₆₀ in the paper [2] above and PbS in the current research. However, after the addition of Ag NPs, NIR light in fact formed the localized surface plasmon effect near the Ag NPs island, enhancing the electric field and making tunneling more obvious, allowing more electrons to participate in carrier transport. From Figure 6d, it can be seen that the threshold voltage changes from 4.4 V to 3.4 V as the NIR light switch turns from off to on, which is consistent with the simulation results discussed above. This phenomenon was also due to the fact that the electric field between Zn_{0.95}Mg_{0.05}O film was strengthened by LSP which contributes to the enhancement of quantum tunneling. Therefore, with the applied voltage maintained at 4 V, a switched UCD could work under excitation of NIR light.

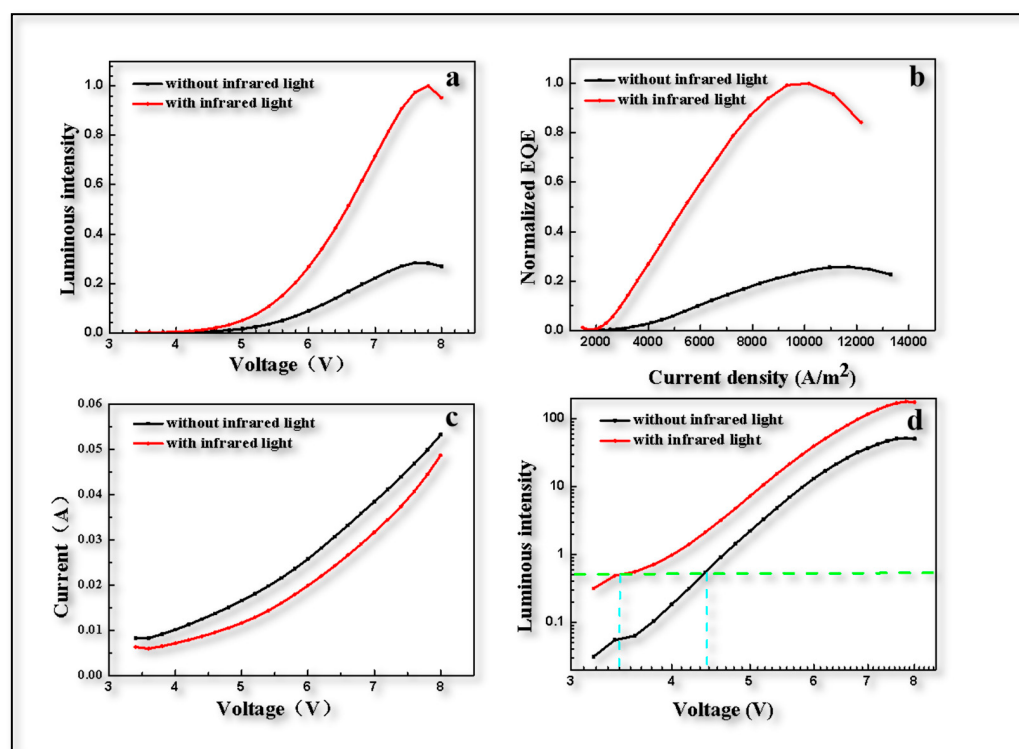


Figure 6. Photoelectric performance test of upconversion device. (a) Value of green light emission intensity of device with voltage change. (b) Normalized EQE varies with current density. (c) I-V curve of current with voltage. (d) Change of switching on voltage of 530 nm green light.

Finally, in order to further prove the electron tunneling mechanism of Zn_{0.95}Mg_{0.05}O thin films, the current–voltage characteristic curve of ITO/Zn_{0.95}Mg_{0.05}O/AgNP/PbS QDs/Ag structure was constructed, as shown in Figure 7a. In metal-oxide-metal and metal-oxide-semiconductor systems, the direct electron tunneling effect can occur if the thickness of the intermediate oxide is less than 4 nm; if the thickness exceeds 4 nm, F-N tunneling is observed [30,31]. We fitted the curve according to F-N tunneling theory, using a ZnO layer thickness of ~100 nm and an electric field strength of ~40 mV/mm, as shown in Figure 7b, which is consistent with the reported F-N curve formula [32]. As a result, it was confirmed that the electrons could be successfully transferred from PbS QDs to the Zn_{0.95}Mg_{0.05}O interface due to energy-bending by the tunneling process. Meanwhile, inducing Ag NPs was beneficial for such a tunneling process due to the LSP effect.

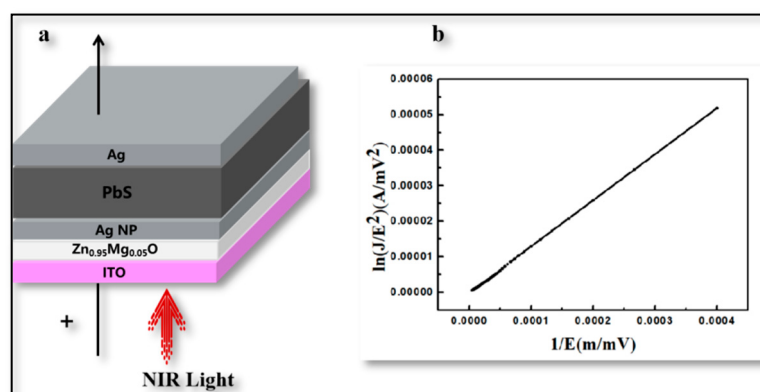


Figure 7. F-N Fitting Results. (a) Schematic cross-sectional view of tunneling structures. (b) Fitting results of ITO/ $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ /Ag NP/PbS QDs/Ag structure.

4. Conclusions

In this paper, a NIR-to-visible upconversion device (UCD) with switching characteristics was fabricated. The device structure was characterized as ITO/ $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ /Ag NPs/PbS QDs/ MoO_x /poly-TPD/(CdSe/ZnS) QDs/ $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ /Ag electrode.

In this structure, we found that, firstly, as PbS film was irradiated by NIR light (1050 nm), hole-electron pairs could be generated and then moved under the horizontal electric field. Electrons could be passed through the barrier between PbS QDs and $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$, leaving holes to transfer from poly-TPD to CdSe/ZnS QDs. Meanwhile, holes could be injected from the ITO electrode and accumulated at the interface between the ITO and $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ layers. Secondly, we found that electrons were injected from the Ag electrode to CdSe/ZnS QDs through the $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ layer; thus, electrons and holes could be combined within CdSe/ZnS QDs as excitons to emit light. Therefore, it was demonstrated that UCD could convert 1050 nm NIR light to 530 nm green light quickly and directly.

It is worth noting that the electrons could be successfully transferred from PbS QDs to $\text{Zn}_{0.95}\text{Mg}_{0.05}\text{O}$ interface due to energy-bending by the tunneling process, which was proved by fitting the F-N quantum tunneling curve of the voltage and current characteristics. Meanwhile, inducing Ag NPs was beneficial for such tunneling processes due to the LSP effect, which can decrease the threshold voltage and increase the brightness of the device under NIR radiation.

This type of UCD has great application potential in the field of optoelectronic devices because it brings more possibilities for facilitating the complicated barrier interfaces.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma16051973/s1>.

Author Contributions: Conceptualization: Y.Z., W.L. and J.C.; Data curation: Y.Z.; Funding acquisition: L.W., W.L. and J.C.; Investigation: Y.Z., X.L., F.X. and J.C.; Methodology: X.L., F.X., J.P. and L.W.; Project administration: J.P., W.L. and J.C.; Resources: Z.W., H.T., F.X., W.L. and J.C.; Software: H.T.; Supervision: C.L. and J.C.; Validation: J.P. and L.W.; Writing—original draft: Y.Z.; Writing—review and editing: C.L. and J.C. All authors have read and agreed to the published version of the manuscript.

Funding: The paper received grants from Leading Technology of Jiangsu Province Basic Research Plan (BK20212006, BK20192003), Ministry of Science and Technology International cooperation projects (2021YFE0105900), The Natural Science Foundation of Jiangsu Province (BK20190774), National Key Research and Development Program of China (2018YFE0125500, 2021YFE0105900), National Natural Science Foundation Project for Young Researcher (12005038), Research Fund for International Young Scientists (62050410350), National Natural Science Foundation Project of China (62175028, 51879042, 61674029, 62205153, 62205152, 12174049, 51972058), Program 111_2.0 in China (BP0719013).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is contained within the article or Supplementary material. For more information, please contact the author Yuyi Zhang (220211715@seu.edu.cn).

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Yang, C.J.; Cho, T.Y.; Lin, C.L.; Wu, C.C. Organic Light-Emitting Devices Integrated with Solar Cells: High Contrast and Energy Recycling. *Appl. Phys. Lett.* **2007**, *90*, 173507. [\[CrossRef\]](#)
2. Kim, D.Y.; Song, D.W.; Chopra, N.; De Somer, P.; So, F. Organic Infrared Upconversion Device. *Adv. Mater.* **2010**, *22*, 2260–2263. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Norton, B.; Eames, P.C.; Mallick, T.K.; Huang, M.J.; McCormack, S.J.; Mondol, J.D.; Yohanis, Y.G. Enhancing the performance of building integrated photovoltaics. *Sol. Energy* **2011**, *85*, 1629–1664. [\[CrossRef\]](#)
4. Wang, X.Z.; Tam, H.L.; Yong, K.S.; Chen, Z.K.; Zhu, F. High performance optoelectronic device based on semitransparent organic photovoltaic cell integrated with organic light-emitting diode. *Org. Electron.* **2011**, *12*, 1429–1433. [\[CrossRef\]](#)
5. Chiu, T.L.; Chang, W.F.; Wu, C.C.; Lin, C.F.; Lee, J.Y.; Liu, S.W.; Chen, C.T.; Lee, J.H. Tandem Organic Light-Emitting Diode and Organic Photovoltaic Device Inside Polymer Dispersed Liquid Crystal Cell. *J. Disp. Technol.* **2013**, *9*, 787–793. [\[CrossRef\]](#)
6. Liu, H.C.; Gao, M.; Poole, P.J. A 1.5 μm Upconversion device. *Electron. Lett.* **2000**, *36*, 1050–1301.
7. Ban, D.; Luo, H.; Liu, H.C.; Wasilewski, Z.R.; SpringThorpe, A.J.; Glew, R.; Buchanan, M. Optimized GaAs/AlGaAs light-emitting diodes and high efficiency wafer-fused optical Upconversion devices. *J. Appl. Phys.* **2004**, *96*, 5243–5348. [\[CrossRef\]](#)
8. Yang, Y.; Shen, W.Z.; Liu, H.C.; Laframboise, S.R.; Wicaksono, S.; Yoon, S.F.; Tan, K.H. Near-infrared photon upconversion devices based on GaNAsSb active layer lattice matched to GaAs. *Appl. Phys. Lett.* **2009**, *94*, 093504. [\[CrossRef\]](#)
9. Kim, D.Y.; Choudhury, K.R.; Lee, J.W.; Song, D.W.; Sarasqueta, G.; So, F. PbSe nanocrystal-based infrared-to-visible Upconversion device. *Nano Lett.* **2011**, *11*, 2109–2113. [\[CrossRef\]](#)
10. Zhou, W.; Shang, Y.; Arquer, F. Solution-processed Upconversion photodetectors based on quantum dots. *Nat. Electron.* **2020**, *3*, 251–258. [\[CrossRef\]](#)
11. Chen, J.; Wang, Q.S. Recent progress of infrared upconversion device based on the integration of OLED. *Chin. J. Opt.* **2005**, *1*, 17–27.
12. Ban, D.; Han, S.; Lu, Z.H. Near-infrared to visible light optical upconversion by direct tandem integration of organic light-emitting diode and inorganic photodetector. *Appl. Phys. Lett.* **2007**, *90*, 1300. [\[CrossRef\]](#)
13. Cheng, Z.Q.; Shi, H.Q.; Yu, P.; Liu, Z.M. Surface-enhanced Raman scattering effect of silver nanoparticles array. *Acta Phys. Sin.* **2018**, *67*, 197302. [\[CrossRef\]](#)
14. Wang, H.B.; Tao, J.; LV, J.G.; Meng, D.J.; Li, Y.; Zhao, Y.Z.; Wang, J.X.; Zhang, J.; Qin, Y.X.; Wang, W.B.; et al. Absorption enhancement of silicon via localized surface plasmons resonance in blue band. *Chin. Opt. Lett.* **2020**, *13*, 1362–1384.
15. Cao, Y.L.; Ding, X.L.; Li, H.C.; Yi, Z.G.; Wang, X.F.; Zhu, J.J.; Kan, C.X. Morphology-Controllable Noble Metal Nanoparticles: Synthesis Optical Property and Growth Mechanism. *Acta Phys. -Chim. Sin.* **2011**, *27*, 1273–1286.
16. Zhao, W.G.; Su, L.; Zhou, Z.N.; Zhang, H.J.; Lu, L.L.; Zhang, S.W. Preparation of Pd/Co Bimetallic Nanoparticles and Their Catalytic Activity for Hydrogen Generation. *Acta Phys. -Chim. Sin.* **2015**, *31*, 145–152.
17. Wang, J.; Wang, W.X. Significance of physicochemical and uptake kinetics in controlling the toxicity of metallic nanomaterials to aquatic organisms. *J. Zhejiang Univ. Sci. A.* **2014**, *15*, 573–592. [\[CrossRef\]](#)
18. Abdi, Y.; Otrooshi, N.; Miri, M.F. Surface plasmon resonance of Ag nanoparticles in the vicinity of a high impedance surface. *Curr. Appl. Phys.* **2014**, *14*, 1567–1739. [\[CrossRef\]](#)
19. Xiu, X.W.; Hou, L.P.; Yu, J.; Jiang, S.Z.; Li, C.H.; Zhao, X.F.; Peng, Q.Q.; Qiu, S.; Zhang, C.; Man, B.Y.; et al. Manipulating the surface-enhanced Raman spectroscopy (SERS) activity and plasmon-driven catalytic efficiency by the control of Ag NP/graphene layers under optical excitation. *Nanophotonics* **2021**, *10*, 1529–1540. [\[CrossRef\]](#)
20. Atta, A.; Abdelhamied, M.M.; Abdelreheem, A.M.; Althubiti, N.A. Effects of polyaniline and silver nanoparticles on the structural characteristics and electrical properties of methylcellulose polymeric films. *Inorg. Chem. Commun.* **2022**, *135*, 109085. [\[CrossRef\]](#)
21. Tagliabue, G.; DuChene, J.S.; Abdellah, M. Ultrafast hot-hole injection modifies hot-electron dynamics in Au/p-GaN heterostructures. *Nat. Mater.* **2020**, *19*, 1312–1318. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Schoeller, H.; Schön, G. Mesoscopic quantum transport: Resonant tunneling in the presence of a strong Coulomb interaction. *Phys. Rev. B.* **1994**, *50*, 18436–18452. [\[CrossRef\]](#)
23. Yang, Z.L.; Liu, Y.Q.; Yang, Y.Q. Extended Q-band fluorescence lifetime of Tetraphenyl porphyrins adsorbed on silver nanoparticles. *Acta Phys. Sin.* **2012**, *61*, 037805.
24. Qiu, W.; Müller, R.; Voroshazi, E.; Conings, B.; Carleer, R.; Boyen, H.-G.; Turbiez, M.; Froyen, L.; Heremans, P.; Hadipour, A. Nafion-Modified MoOx as Effective Room-Temperature Hole Injection Layer for Stable, High-Performance Inverted Organic Solar Cells. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3581–3589. [\[CrossRef\]](#) [\[PubMed\]](#)

25. Zhang, Y.Q.; He, Z.Y.; Du, X.Y.; Han, J.Y.; Lin, H.; Zheng, C.J.; Wang, J.; Yang, G.; Tao, S.L. High-performance organic upconversion device with 12% photon to photon conversion efficiency at 980 nm and bio-imaging application in near-infrared region. *Opt. Express*. **2022**, *30*, 16644–16654. [[CrossRef](#)]
26. Li, D.W.; Hu, Y.S.; Zhang, N.; Lv, Y.; Lin, J.; Guo, X.Y.; Fan, Y.; Luo, J.S.; Liu, X.Y. Near-Infrared to Visible Organic Upconversion Devices Based on Organic Light-Emitting Field Effect Transistors. *ACS Appl. Mater. Interfaces* **2017**, *41*, 36103–36110. [[CrossRef](#)]
27. Kim, Y.; Park, B. Photo-persistent effect-induced energy band bending at the TiO₂/Ag nanoparticle surface plasmonic interface. *Mater. Lett.* **2022**, *316*, 132001. [[CrossRef](#)]
28. Miao, J.; Zhang, F. Recent progress on photomultiplication type organic photodetectors. *Laser Photon. Rev.* **2019**, *13*, 1800204. [[CrossRef](#)]
29. Chen, C.C.; Lu, Y.H. Local Surface plasmon in Nonspherical Metal Nanoparticles. *Chin. Phys. Lett.* **2007**, *24*, 4.
30. Dahlke, W.E.; Sze, S.M. Tunneling in metal-oxide-silicon structures. *Solid-State Electron.* **1967**, *10*, 865–873. [[CrossRef](#)]
31. Zhu, Y.Y.; Fang, Z.B.; Chen, S. Fowler-Nordheim hole tunneling in metal-Er₂O₃-silicon structures. *Appl. Phys. Lett.* **2007**, *91*, 122914. [[CrossRef](#)]
32. Lenzlinger, M.; Snow, H. Charge transport and storage in metal-nitride-oxide-silicon (MNOS) structures. *J. Appl. Phys.* **1969**, *40*, 3307–3319.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.