Hot Electron-Based Solid State TiO$_2$|Ag Solar Cells

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The present work reports a simple and direct sputtering deposition to form solid state TiO$_2$|Ag independent plasmonic solar cells. The independent plasmonic solar cells are based on a Schottky barrier between two materials, TiO$_2$ and Ag. The Ag functions as the absorber generating “hot” electrons, as well as the contact for the solar cell. The Ag sputtering is performed for different durations, to form Ag nanoparticles with a wide size distribution on the surface of rough spray pyrolysis deposited TiO$_2$. Incident photon to current efficiency (IPCE) measurements show photovoltaic activity below the TiO$_2$ bandgap, which is caused by the silver nanoparticles that have a wide plasmonic band, leading to the generation of “hot” electrons. X-ray photoelectron spectroscopy analysis supports the “hot” electron injection mechanism by following the Ag plasmon band and detecting local photovoltages. The measurements show that electrons are formed in the Ag upon illumination and are injected into the TiO$_2$, producing photovoltaic activity. J–V measurements show photocurrents up to 1.18 mA cm$^{-2}$ and photovoltages up to 430 mV are achieved, with overall efficiencies of 0.2%. This is, to our knowledge, the highest performance reported for such independent plasmonic solar cells.

1. Introduction

Plasmonic solar cells, which are one of the presently researched photovoltaic systems,[1] contain metallic nanoparticles that are utilized for electron generation or for light trapping and scattering in the solar cells. The importance of the plasmonic effect on photovoltaics is that it improves basic processes within solar cells such as electron generation and injection, charge separation, and reducing recombination. The presented research focuses on plasmonic photovoltaics as absorbers for generating and injecting electrons, unlike most of the research in the plasmonic solar cell field. The basic operation of the discussed solar cells, including formation of charge carriers, is due to the plasmonic effect in the cells, and is not just supported or enhanced by it.

The operation of plasmonic solar cells is dependent upon the optical excitation of surface plasmons, which are collective oscillations of the surface electronic cloud in metallic nanoparticles. One of the important characteristics of metallic nanoparticles is the coupling interaction of their plasmonic oscillations with incident photons of the same frequency; this coupling excites surface plasmon resonance (SPR).[2] The SPR gives rise to strong electromagnetic fields, which can be used for trapping or reflecting light, enhancing photovoltaic activity,[3] surface-enhanced Raman spectroscopy (SERS),[3] and photo-catalysis.[4] When the surface plasmon decays to the ground state it can cause electron excitation within the metallic nanoparticle itself, the excited electrons are often referred to as “hot” electrons. The “hot” electrons are highly active nonequilibrium electrons that have sufficient kinetic energy to overcome potential barriers, or tunnel through thin layers of semiconductors.[5] Since the “hot” electrons are energetic they can be used in conjunction with a semiconductor, to form a Schottky barrier photovoltaic device. As the absorption and excitation of the SPR is very wide and extends beyond the visible range of the solar spectrum, depending on the material and structure, the “hot” electrons that are formed can extend the spectral response of the photovoltaic device. The “hot” electrons are directly injected into the conduction band of the semiconductor, forming and improving the photovoltaic activity.

One of the semiconductors that is used extensively for renewable energy applications is TiO$_2$, which is a wide bandgap (3.2 eV) metal oxide semiconductor. As it is a highly n-type material, it is utilized as an electron conducting layer in solar cells to help with charge separation,[6] or as a photocatalyst for water splitting.[7] The wide bandgap of the TiO$_2$ only allows it to be used for solar cells in conjunction with an absorbing material, be it dye, quantum dots, or other materials, since by itself it would only absorb light from the UV part of the solar spectrum. To improve or form the photovoltaic activity of the TiO$_2$ as an independent photovoltaic system, silver metallic nanoparticles or nanostructures can be used. The metallic nanoparticles form a Schottky barrier solar cell with the TiO$_2$, and the “hot” electrons that have enough kinetic energy to overcome the Schottky barrier height are injected into the TiO$_2$, as
The use of Ag nanoparticles as the active absorbing layer with TiO₂ for independent plasmonic solar cell applications was proposed by Tian and Tatsuma, who demonstrated plasmon-induced photoelectrochemistry of nonporous TiO₂ decorated with Ag and/or Au nanoparticles. Incident photon to current efficiency (IPCE) of ≈4% (at ≈430 nm) was achieved for TiO₂ decorated with Ag nanoparticles, measured in a NaOH aqueous solution. In another investigation, glutathione protected silver and gold nanoclusters were used to sensitize TiO₂ in the same setup as DSSCs, using an electrolyte and Pt counter electrode. The Ag nanocluster sensitized solar cell gave a short circuit current of ≈40 µA cm⁻² and an open circuit voltage of 270 mV, while the Au–Ag composite nanocluster solar cell gave higher performances. Other work showed the synthesis of Ag nanocluster and TiO₂ composite thin films, which obtained photocurrents of ≈20 µA cm⁻². In this study the photoelectrochemical mechanism that was proposed involved SPR photoexcited electrons, which were injected into the TiO₂ conduction band.

In all the investigations mentioned above, there is always use of an electrolyte and the solar cell structure is photoelectrochemical. As the Ag nanoparticles inject a “hot” electron into the TiO₂ conduction band, the Ag becomes oxidized, and is left with a hole (positively charged). The Ag nanoparticle is reduced back to its original state by electrons from the electrolyte in the wet electrochemical setup. However, efforts have been made to turn the TiO₂ and Ag nanoparticle solar cell into a solid state device. Takahashi et al. used an Al₂O₃ nanomask to deposit Ag nanoparticles on top of a TiO₂ layer on one side, and deposited indium tin oxide (ITO), which served as the conductive layer on the other side of the nanoparticles, achieving an IPCE of ≈0.6%. More recently, Reineck et al. prepared solar cells by self-assembly of 25 nm Ag nanoparticles on TiO₂, with Spiro-OMeTAD as the hole conducting layer on top of the Ag particles. Using accelerated lifetime testing (under 505 nm LED illumination), an average photocurrent of ≈550 µA cm⁻² was demonstrated. In both of the aforementioned cases no current density–voltage (J–V) curves were given to support the photovoltaic activity of the cells.

In the present research, we show that “hot” electrons are generated in silver nanoparticles that spontaneously form during sputtering on TiO₂ prepared by spray pyrolysis. The formation of the Ag nanoparticles, which have a large size distribution, is achieved without complicated deposition techniques, and is due to the rough nature of the TiO₂ layer. The method used in the investigation is the combinatorial material science approach, which utilizes combinatorial fabrication methods and high-throughput characterization tools. Combinatorial material science has been used in the past to investigate electronic materials, new magnetic materials, catalysts, and solar cells but has not been used to study plasmonic-based solar cells, and specifically TiO₂/Ag independent plasmonic solar cells. To investigate
these solar cells, the silver was deposited with different thicknesses using radio frequency (RF) sputtering. We characterize the resulting TiO\textsubscript{2}/Ag independent plasmonic solar cells using a combination of photoemission and combinatorial techniques. The former is used to confirm the “hot” electron mechanism for generation of the photoactivity and to develop a band diagram of our solar cells. The “hot” electron mechanism in the solid state TiO\textsubscript{2}/Ag solar cell is regenerative, and can operate in a closed circuit without the addition of a hole-transporting material. We utilize \( J-V \) measurements to show how the performance of our solar cells varies with Ag deposition times. Using IPCE measurements, we provide evidence that the “hot” electron mechanism is supported by an enhancement of the photoresponse of the solar cells into the visible region of the solar spectrum. The best cell performances give short circuit currents up to 1.18 mA cm\(^{-2}\) and are shown in Figure \( S2 \) (see Experimental Section). The thicknesses of TiO\textsubscript{2} and varying thicknesses of the silver. Initially, a linear thickness gradient of TiO\textsubscript{2} was deposited using spray pyrolysis. Then, the Ag was sputtered for different durations through a shadow mask with a 13 \( \times \) 13 grid of round holes onto the library, where each row has a different thickness. The resulting library contained 169 solar cells differing from each other by their TiO\textsubscript{2}:Ag ratio. Each of the cells in the library was characterized using high-throughput techniques. Table \( S1 \) shows the thickness of the TiO\textsubscript{2} as analyzed by the optical measurements. The thicknesses of the Ag points were estimated based on the sputtering parameters, and are shown in Table 1 (see Experimental Section). The first row (numbered 1) has the least amount of Ag, and the amount of Ag increases with each row.

**Table 1.** Sputtering deposition time and estimated Ag thickness for each row of the library, the library structure is shown in Figure 2. The Ag points that were analyzed beyond the typical \( J-V \) characterizations are marked by an asterisk in the table, and mark the points that were further measured by XPS, SEM, and IPCE.

| Row | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|-----|---|---|---|---|---|---|---|---|---|----|----|----|----|
| Deposition time [s] | 20 | 40 | 60 | 80 | 120 | 160 | 200 | 240 | 320 | 400 | 480 | 560 | 640 |
| Ag thickness [nm] | 5 | 10 | 15 | 20 | 30 | 40 | 50 | 60 | 80 | 100 | 120 | 140 | 160 |
| XPS | * | * | * | * | * | * | * | * | * | * | * | * | * |
| SEM and particle size analysis | * | * | * | * | * | * | * | * | * | * | * | * | * |
| IPCE | * | * | * | * | * | * | * | * | * | * | * | * | * |

The SPR occurs in metallic nanoparticles, and as such it is critical that the silver nanoparticles are in the metallic Ag\(^0\) state, and not in one of the oxidized states. In order to rule out the formation of silver oxides in the silver patches and check that the Ag does not penetrate into the TiO\textsubscript{2}, X-ray photoelectron spectroscopy (XPS) and Rutherford Backscattering (RBS) were performed. Bare TiO\textsubscript{2} and points with Ag film thicknesses of 10 and 100 nm (rows 2 and 10, respectively) were measured by XPS, as seen in Figure 3. Figure 3a presents XPS results for the Ti 2p core level. The Ti 2p\textsubscript{3/2} peak position is 459.24 eV representing the Ti\(^{4+}\) oxidation state, as expected for TiO\textsubscript{2}. The binding energy of the Ag 3d\textsubscript{5/2} core level is 368.30 eV (Figure 3b), indicative of the Ag\(^0\) metallic state. The peak positions for oxidized silver, being mainly Ag\(\textsubscript{2}O\) or Ag\(\textsubscript{2}O\), have been reported for binding energies of 367.8–368 and 367.3–367.6 eV, respectively.\(^{[23]}\) hence there is probably a small amount of oxidized Ag in the library, and only on the top surface, no other Ag species (such as sulﬁdes) were seen at all. The inset in Figure 3b shows a widespread plasmonic peak for the silver, as a function of its energetic distance from the Ag 3d\textsubscript{5/2} peak. The plasmonic peak, which also supports that metallic silver was obtained, ranges from binding energies of 370.6–372.8 eV (distance from

**Figure 2.** Schematic of the structure of the studied library containing 169 separate solar cells. The TiO\textsubscript{2} layer was deposited as a linear gradient by spray pyrolysis on a glass slide (72 mm \( \times \) 72 mm) coated with FTO layer (transparent conductive oxide). The Ag is deposited on top of the TiO\textsubscript{2} layer by sputtering, using a shadow mask with 169 holes. The thickness changes of the TiO\textsubscript{2} and Ag layers are indicated in the scheme. The TiO\textsubscript{2} is thickest on the left side of the library, with a linear decrease in thickness to the right side of the library (Figure S5b, Supporting Information). The Ag has the lowest thickness in row 1 (shortest deposition time) with the highest thickness being in row 13 (longest deposition time). The Ag forms as thin nanoparticle films, and the cones are only used to depict the different thicknesses.

**2. Results and Discussion**

The plasmonic solid state TiO\textsubscript{2}/Ag independent solar cells were studied with a combinatorial approach. Figure 2 shows the schematic configuration of a combinatorial library with varying thicknesses of TiO\textsubscript{2} and varying thicknesses of the silver. The plasmonic solid state TiO\textsubscript{2}/Ag independent plasmonic solar cells were utilized using a combination of photoemission and combinatorial techniques. The former is provided evidence that the “hot” electron mechanism is supported by an enhancement of the photoresponse of the solar cells into the visible region of the solar spectrum. The best cell performances give short circuit currents up to 1.18 mA cm\(^{-2}\) and are shown in Figure 2. The TiO\textsubscript{2} layer was deposited as a linear gradient by spray pyrolysis on a glass slide (72 mm \( \times \) 72 mm) coated with FTO layer (transparent conductive oxide). The Ag is deposited on top of the TiO\textsubscript{2} layer by sputtering, using a shadow mask with 169 holes. The thickness changes of the TiO\textsubscript{2} and Ag layers are indicated in the scheme. The TiO\textsubscript{2} is thickest on the left side of the library, with a linear decrease in thickness to the right side of the library (Figure S5b, Supporting Information). The Ag has the lowest thickness in row 1 (shortest deposition time) with the highest thickness being in row 13 (longest deposition time). The Ag forms as thin nanoparticle films, and the cones are only used to depict the different thicknesses.
The energy of the surface plasmon peak depends on the size and shape of the silver nanoparticles from which it arises. Notably, the corresponding XPS signal is broad, with a pronounced extension to low energies, as compared to the typical bulk plasmon of silver at 3.8 eV. Therefore this broad XPS signal reflects the presence of a broad band of plasmonic modes, which is typical to nanoparticles in general and, possibly, also to the size and shape distribution of these nanoparticles.

To further confirm the existence of Ag and to check if the Ag penetrates into the TiO₂ film, RBS measurements were performed (Figure S1, Supporting Information). The results for the RBS measurements show a sharp surface peak for the Ag that does not overlap with the TiO₂ layer beneath it, meaning that there is no penetration of Ag into the TiO₂ layer and that the silver at the TiO₂-Ag interface did not oxidize. Moreover, composition calculations show 100% of silver atoms for the surface peak and no indication to the presence of oxygen atoms, signifying that the Ag is probably metallic, although the presence of an oxidized layer on top of the surface of the Ag patches is not completely ruled out.

Ag 3d₅/₂ peak is 2.3–4.5 eV). The energy of the surface plasmon peak depends on the size and shape of the silver nanoparticles from which it arises. Notably, the corresponding XPS signal is broad, with a pronounced extension to low energies, as compared to the typical bulk plasmon of silver at 3.8 eV. Therefore this broad XPS signal reflects the presence of a broad band of plasmonic modes, which is typical to nanoparticles in general and, possibly, also to the size and shape distribution of these nanoparticles.

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The library was measured by high resolution scanning electron microscopy (HRSEM), and cross sections were prepared and measured by a focused ion beam scanning electron microscope (FIB-SEM) to determine the structural surface and cross sectional morphology of the TiO₂ and Ag films. As can be seen in the top left of Figure 4, the surface of the bare TiO₂ layer is very rough (~50–60 nm variations), which is due to the spray pyrolysis deposition method, following the FTO surface roughness. The Ag nanoparticles, which form on the TiO₂ layer, have a wide size distribution (Figure S3, Supporting Information), and form preferentially on the sides and edges of the TiO₂, which may represent high energy TiO₂ atomic planes, that favor the Ag deposition.[24] The TiO₂ surface roughness and structuring can explain the formation of the Ag nanoparticles, as shown in the top right of Figure 4, for the 60 s deposition time (15 nm). The nanoparticles spontaneously form during the sputtering deposition on the rough surface of the TiO₂, and are not homogeneous in size or shape and do not completely cover the TiO₂ surface. Energy-dispersive X-ray spectroscopy (EDS) measurements, shown in Figure S2 and Table S1 (Supporting Information), were performed to check for the presence of Ag on the TiO₂ coated with the nanoparticles. The produced silver nanoparticles confirm the assumption that the broad Ag plasmonic peak, observed in the XPS measurements, is due to the many plasmonic modes originating from the variety in size and shape distribution of the Ag nanoparticles. When increasing the deposition time further to 480 s (120 nm, Figure 4 bottom left), a thin layer of the Ag is formed. This layer is still comprised of nanoparticles, and has a nanostructured and rough nature, due to the surface structuring of the TiO₂, as can be seen in the cross section FIB-SEM image (Figure 4 bottom right). The cross section shows that the silver morphology is dictated by the surface roughness of the TiO₂ layer. As such, when small amounts of Ag are deposited, nanoparticles form on the TiO₂, and when large amounts of Ag are deposited, nanostructured thin films are formed. These results indicate that it can be simple to pattern nanoparticle on a rough surface, using direct deposition methods such as sputtering.

For photovoltaic analysis, the J–V characteristics of the library were measured. There is high photovoltaic activity for the library, given that the absorber materials are small metallic nanoparticles on the surface of TiO₂. As shown in the photovoltaic maps in Figure 5a, the short circuit currents (Jₛₛ), open circuit voltages (Vₒₒ), fill factors (FF), and maximum powers (Pₘₘₐₓ) all increase with Ag deposition time up to 480 s (120 nm,
row 12, Figure 2). In Figure 5a, short circuit currents of up to 750 µA cm$^{-2}$, and open circuit voltages of 430 mV are achieved. The FFs exceed 60% and the $P_{\text{max}}$ reaches 100 µW cm$^{-2}$. The increase of the photocurrents, as a function of Ag deposition time (nanostructured Ag film thickness), is caused either by the higher amount of absorbing material or by the fact that the particles start connecting to each other at higher deposition times. When there is more silver, a larger amount of SPR occurs, leading to more “hot” electrons being generated and injected into the TiO$_2$. While the higher deposition times also lead to better interconnections between Ag nanoparticles and hence better conductivity, there is also much more SPR in the thick Ag layers that is the main contributor to the better performance in these thicknesses. It is highly probable that since the Ag nanoparticles in the shorter deposition times have almost no interconnections between them that the conductivity is low. In a separate deposition of 400 s (100 nm) of Ag on TiO$_2$, short circuit currents of 1.18 mA cm$^{-2}$, and open circuit voltages of ≈380 mV are attained (Figure 5b). The energy conversion efficiency ($\eta$) of this solar cell is 0.2%, which is the highest efficiency that has been achieved, as far as we know, for a solid state TiO$_2$|Ag independent Schottky barrier “hot” electron plasmonic solar cell. These results are particularly interesting considering no hole transport layer was introduced in the solar cells, and they are manufactured in a simple direct method, removing the necessity of special templating or lithography steps needed to form the nanoparticles.

To determine the source of the photovoltaic activity, the IPCE of several cells in the TiO$_2$|Ag library were measured (Figure 6) along the center column of the library (Figure 2). The results clearly indicate a peak corresponding to the Ag nanoparticle SPR band ranging from 400–450 nm (Figure 6a), with an onset at ≈700 nm. This SPR active band does not belong to the TiO$_2$ as its optical absorption onset starts at about 380 nm. The peak seen between 400 and 450 nm, with an onset at ≈600 nm, corresponds very well with the range of plasmonic energies that are observed by XPS (inset Figure 3b). Similar IPCE peaks, at about 460 nm with an onset at ≈600 nm, have been seen in the past for self-assembled Ag nanoparticles on TiO$_2$.[18] In that research the nanoparticle diameters were in between 10 and 50 nm, with an average diameter of 25 nm. Whereas here, the rough surface of the TiO$_2$ enables the formation of silver nanoparticles with various sizes and shapes. The smallest Ag particle diameters are less than 5 nm, while the largest nanoparticles reach sizes of ≈500 nm (Figure S3, Supporting Information). The large size variation, between the Ag nanoparticles is probably the cause of the wide IPCE active range, from 400 to 700 nm. The IPCE values increase with the size of the Ag nanoparticles and reach 1.4%. The higher IPCE values for the larger Ag thicknesses confirm that when there are more plasmonic absorbers in the solar cells then more “hot” electrons are formed, leading to better photovoltaic performance, which is seen in the $J_{\text{sc}}$ results (Figure 5a). Further evidence for the role of surface plasmons is provided by the fact that the IPCE peak shifts toward...
longer wavelengths as the thickness of the Ag (based on deposition time and rate) increases (Figure 6b). The particle size analysis, seen in Figure S3 (Supporting Information), shows an increase in the general size as the deposition time grows. Thus the IPCE peak shift is attributed to the growth in the average size of the nanoparticles with increase of the Ag deposition time, and is verified in two different libraries (prepared using the same methods). According to the Mie theory, there is a redshift of plasmonic absorption of nanoparticles as they increase in size, supporting the observed results.

To further confirm the “hot” electron injection mechanism behind the photovoltaic activity, XPS-based chemically resolved electrical measurements (CREM) were performed. The measurements were conducted under dark conditions, and then under illumination of a halogen lamp. By evaluating the line shifts we could then learn about the local changes in electrostatic potential and, importantly, compare the values extracted for the silver and TiO2. The photo-response of the Ag 3d5/2 peak, given in Figure 7a, shows good reversibility of the Ag line shift, indicating that the photovoltage developing at the silver is nearly...
TiO\textsubscript{2} causes the Fermi energy in the silver to shift down from nanoparticles. The “hot” electron injection from the Ag into the vacuum is caused by electrons being removed from the silver in the Fermi energy, relative to the vacuum level, upon illumination. This results in the Fermi energy level shifting downwards. The increase in band minimum (CBM) for the bare TiO\textsubscript{2}, indicative of a separation places the Fermi level diagrams as derived for bare TiO\textsubscript{2} and for the TiO\textsubscript{2}|Ag independent plasmonic solar cell. The TiO\textsubscript{2} has a band bending that is larger than 170 meV, which corresponds to the \( V_{oc} \) values that are achieved. Both the measured energy band alignment and the TiO\textsubscript{2} band bending support the “hot” electron injection mechanism that is purposed.

Figure 7. a) XPS measurements of the Ag 3d\textsubscript{3/2} core level, under dark conditions and under halogen lamp illumination, where both dark measurements overlap exceedingly well (black and red curves). The results show a shift of the Ag 3d\textsubscript{3/2} peak under illumination to lower binding energies, indicating an increase in the Fermi energy when the Ag is illuminated. The increase in Fermi energy shows that electrons are injected from the Ag into the TiO\textsubscript{2} upon illumination. b) Energy band diagram of the bare TiO\textsubscript{2} library, showing that the TiO\textsubscript{2} is highly n-doped. c) Energy band alignment diagram of the TiO\textsubscript{2}|Ag solar cell. The TiO\textsubscript{2} has a band bending that is larger than 170 meV, which corresponds to the \( V_{oc} \) values that are achieved. Both the measured energy band alignment and the TiO\textsubscript{2} band bending support the “hot” electron injection mechanism that is purposed.

A schematic presentation of the proposed energy band diagrams as derived for bare TiO\textsubscript{2} and for the TiO\textsubscript{2}|Ag independent plasmonic solar cell is shown in Figure 7b,c. The band diagrams are based on XPS measurements given in Figures S4 (Supporting Information), and bandgap calculations\(^{[21]}\) given in Figure S5a (Supporting Information). The TiO\textsubscript{2} bandgap was taken as 3.28 eV, which is an average value of all the points in the library (Figure S5a, Supporting Information). For bare TiO\textsubscript{2} (Figure 7b), the separation energy of the Fermi level (\( E_{F} \)) and of the valence band maximum (VBM), \( E_{VBM} \), is 3.25 eV, in agreement with previous reports.\(^{[28]}\) The energy separation places the Fermi level \( E_{F} = 0.03 \) eV below the conduction band minimum (CBM) for the bare TiO\textsubscript{2}, indicative of a highly n-doped TiO\textsubscript{2} layer. In Figure 7c, the energy band alignment of the TiO\textsubscript{2}|Ag independent plasmonic solar cell is presented. We used the measured work function of the 100 nm Ag cells as the work function of the Ag, since at this Ag thickness the TiO\textsubscript{2} is completely covered by the nanostructured Ag film. The Ti core level spectra of the bare TiO\textsubscript{2}, and after the deposition of 10 nm reveal a binding energy shift average of 170 meV (the shifts are seen from 120 meV to 220 meV), corresponding to band bending of the same amount. For the 100 nm Ag point, we were unable to accurately measure the Ti 2p binding energy, as the Ti signal was attenuated by the high Ag surface coverage. Based on these results, we suggest that the band bending of the TiO\textsubscript{2}|Ag system is at least 170 meV or greater, since it is probable the band bending continued to increase with further Ag deposition but could not be measured here. Given that the measured \( V_{oc} \) in Schottky barrier solar cells is limited by the barrier height we can use the \( J–V \) measurements to ascertain the band bending for higher Ag thickness cells. The 10 nm Ag solar cells exhibit a \( V_{oc} \) of \( \approx 160 \) mV, in agreement with the band bending we measure. Moreover, the 100 nm Ag solar cells show a higher \( V_{oc} \) of \( \approx 350–400 \) mV that support the CREM work function measurements, which show an increase of 480 meV.

Overall the energy band alignment, including the band bending for the TiO\textsubscript{2}|Ag solar cells, based on the CREM is in favor of formation of a Schottky barrier between the rough TiO\textsubscript{2} and the nanostructured Ag film (Figure 7c). The Ag, which is directly deposited by sputtering on the rough TiO\textsubscript{2} surface, plays a triple role in TiO\textsubscript{2}|Ag solar cells. First, the Ag forms a Schottky barrier with the TiO\textsubscript{2}. Second, the Ag performs as the back contact material for the solid state TiO\textsubscript{2}|Ag devices, conducting the holes formed in the solar cells to the electrical contacts. Third, the Ag nanoparticles absorb the incoming light by exciting SPR. The SPR then decays to its original ground state and on the way it excites “hot” nonequilibrium electrons that can be injected into the TiO\textsubscript{2}, producing photocurrent and photovoltaic activity. “Hot” electron injection into the TiO\textsubscript{2} was reported to be very fast, occurring within 50 fs of their formation, for gold nanoparticles without a hole transport layer.\(^{[29]}\) The formation of “hot” electrons in silver nanoparticles is very fast and is on the order of less than 30 fs,\(^{[30]}\) whereas electron–electron scattering and thermalization occur in approximately
100 fs. From the reported timescales, we suggest that in our solar cells, which contain no hole transport layer, the “hot” electron injection from the Ag into the TiO₂ happens on time scales between 30 and 100 fs. The addition of the hole transport material may further improve our TiO₂/Ag solar cells, and help decrease injection times, while preventing the recombination of “hot” electrons in the Ag with oxidized silver atoms that are close to them.

3. Conclusion
In this research, we have demonstrated a simple and direct method for forming TiO₂/Ag independent plasmonic solar cells. The silver was deposited by sputtering, with varying durations, on a rough TiO₂ surface, forming a Schottky junction between the two. The use of sputtering has advantages like controlled deposition times and the removal of complicated templating techniques to form the Ag nanoparticles. The Ag was shown to form metallic nanoparticles, which indicates that it has plasmonic absorptions that lead to SPR. The decay of the SPR excites nonequilibrium electrons, known as “hot” electrons in the Ag, which are injected into the TiO₂, producing photocurrent. The observed photovoltaic activity is high, with the best solar cells reaching efficiencies of 0.2%, which to our knowledge have not been achieved so far for this type of solar cell. The source of the “hot” electrons is the wide IPCE active band edge have not been achieved so far for this type of solar cell.

4. Experimental Section
4.1. Library Preparation
4.1.1. Synthesis of TiO₂ Layer: The TiO₂ thin film layer was deposited by a home-built spray pyrolysis system on a commercially available fluorine doped tin oxide (FTO) coated glass substrate, TEC 15 (72 mm × 72 mm, Hammond Glass Co., Inc.). The glass substrate was cleaned in a sonication bath with soap and deionized water then rinsed in dry ethanol, and washed again with deionized water. The substrate was then treated with Ar plasma for 5 min (PLASMA-PREEN II-862, Plasmatic Systems, Inc.). The glass substrate was placed on a preheated hotplate (Harry Gestigkeit GmbH) heated to 450 °C. The spray pyrolysis system set-up consists of a 3-axis CNC robot (EAS GmbH), a Son-o-tek 120 KHz ultrasonic spraying nozzle, and a syringe pump (New Era Pump Systems, Inc.) for pumping the precursor solution. The TiO₂ precursor solution was prepared by mixing 7.5 mL of titaniumtetraisopropoxide (TTiP, Sigma-Aldrich) and 5 mL of acetylacetone (Sigma-Aldrich) in 240 mL of ethanol (Carlo Erba Reagents), and its pH was 6.8. The precursor carrier gas was filtered dry clean air, and the flow rate was kept at 50 mL h⁻¹. The precursor solution was sprayed using a program that was set to form a linear thickness gradient of the TiO₂ layer, with thicknesses varying from 165 to 440 nm (Figure S5a, Supporting Information).

4.1.2. Deposition of Ag Layer: The silver nanostructured thin films were prepared by RF magnetron sputtering (AJA International Inc.). To deposit the Ag, a shadow-mask with an array of 13 × 13 round holes with a diameter of 1.8 mm, was placed on the substrate with the TiO₂ layer. The sputtering system was pumped down to a base pressure of 1.4 × 10⁻⁷ torr. The silver was deposited from a 2° Ag target (99.99%, Testbourne Ltd) under Ar gas at a flow rate of 30 sccm, and the total pressure in the chamber was 2 mtorr. The target power was kept at 100 W, and the substrate temperature was 23 °C. The deposition time and calibrated Ag thicknesses (Table 1) were calculated based on a deposition rate of 2.4 Å s⁻¹, which was measured by a quartz microbalance. In order to deposit the silver thickness gradient, each row of the shadow-mask (Figure 2) was exposed separately for different sputtering times, as shown in Table 1. The deposited Ag thicknesses varied from 5 to 160 nm.

4.2. Material Characterization
4.2.1. Morphology and Surface Structuring of TiO₂ and Ag: The surfaces of the bare TiO₂ and of the TiO₂ coated with Ag were characterized by a field-emission Helios 600 high resolution electron microscope (HRSEM, FEI). The energy-dispersive X-ray analysis (EDS) in the HRSEM was executed by an 80 mm² X-max detector (Oxford Instruments). Cross section images of the TiO₂/Ag library were taken using a Focused Ion Beam Helios 600 scanning electron microscope system (FEI). Images were taken for points with Ag deposition times of 60 s and 480 s.

4.2.2. Chemical and Electrical Analysis: X-ray photoelectron spectroscopy (XPS) and chemically resolved electrical measurements (CREM)[26b,32] were performed using a Kratos AXIS-Ultra-DLD spectrometer, with a monochromated Al kα x-ray source, applied at low power values, 15–75 W. Core level spectra, work functions, and valence band onsets were measured at selected points on the library with Ag thicknesses of 10 and 100 nm. A bare TiO₂ reference sample was measured as well. The stability of samples under the x-ray irradiation was continuously followed, including minor charging effects. Electrical properties of the samples were further investigated by applying light illumination, using a 250 W halogen lamp at 3200 K (KL 1500 LCD, SCHOTT), equipped with a set of low-pass filters. All measurements correspond to long timescales, on the order of 100–1000 s.

4.3. Solar Cell Device Characterization
4.3.1. Solar Cell Current Density–Voltage (J–V) Characterization: The J–V characteristics of 169 solar cells were measured with a home-built automated scanning j–v system described in depth in our previous reports [6a,21] in order to make an electrical contact to the FTO, a metal frame was ultrasonically soldered around the library edges. The library was illuminated using a xenon laser-driven light source (LDLS, EQ-99FC, ENERGETIQ), which was calibrated to the emission of AM1.5G. The source meter for the J–V electrical measurements was a Keithley 2400. The J–V curve was measured twice, in ascending and descending scan directions, for all the points. The ascending and descending measurements were made to eliminate cells with excessive capacitance. Solar cells that had a less than a 15% difference between the ascending and descending were defined as photovoltaic, and the rest of the points are not analyzed or discussed in this work.

4.3.2. Quantum Efficiency Measurements (IPCE): IPCE measurements were carried out on a Solar Cell Quantum Efficiency Measurement System (Model QEX10, PV Measurements Inc.). The IPCE was measured in AC mode with a bias halogen white light. The IPCE calibration was performed using a slanded certified Si photodiode. The Chopper frequency was set to 4 Hz, and the perturbing light was
a monochromatic Xe lamp. The measurement range was between 350 and 1000 nm, and the measurement step was 5 nm. The center column on the library (same TiO2 thickness, Figure 2) was measured, in order to see the dependence of the IPCE on the Ag thickness.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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