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# Zr-doped TiO<sub>2</sub> as a thermostabilizer in plasmon-enhanced dye-sensitized solar cells

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**Abstract.** Harvesting solar energy is a promising solution toward meeting the world's ever-growing energy demand. Dye-sensitized solar cells (DSSCs) are hybrid organic–inorganic solar cells with tremendous potential for commercial application, but they are plagued by inefficiency due to their poor sunlight absorption. Plasmonic silver nanoparticles (AgNPs) have been shown to enhance the absorptive properties of DSSCs, but their plasmonic resonance can cause thermal damage resulting in cell deterioration. Hence, the influence of Zr-doped TiO<sub>2</sub> on the efficiency of plasmon-enhanced DSSCs was studied, showing that 5 mol.% Zr-doping of the photoactive TiO<sub>2</sub> material can improve the photovoltaic performance of DSSCs by 44%. By examining three different DSSC designs, it became clear that the efficiency enhancing effect of Zr strongly depends on the proximity of the Zr-doped material to the plasmonic AgNPs. © 2017 Society of Photo-Optical Instrumentation Engineers (SPIE) [DOI: [10.1117/1.JPE.7.035504](https://doi.org/10.1117/1.JPE.7.035504)]

**Keywords:** solar cells; dye-sensitized solar cells; Ag nanoparticles; plasmonics; thermostabilization; titania; TiO<sub>2</sub>; Zr-doping.

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## 1 Introduction

Dye-sensitized solar cells (DSSCs) are regarded as one of the most promising solar cell designs among third-generation photovoltaic (PV) technologies, particularly due to their low cost, easy preparation, and minor environmental impact with respect to earlier generation devices.<sup>1,2</sup> The photoactive semiconductor material is typically TiO<sub>2</sub> in nanoparticle (NP) form (nTiO<sub>2</sub>). Advances in their design,<sup>3–5</sup> their incorporation into flexible substrates,<sup>6–9</sup> and their scalable fabrication techniques<sup>10,11</sup> have allowed DSSCs to move from the laboratory scale to real-life application. Although DSSC's positive inherent features can facilitate their entry into the PV market, there is still a need for improvement to achieve higher performance. In other words, an increase in DSSC efficiency is desired. One of the major challenges for efficiency enhancement is the inefficient sunlight absorption in DSSCs.<sup>12</sup> The dye that sensitizes the TiO<sub>2</sub> photo-absorbing material does not respond equally well to all incoming wavelengths of the solar spectrum,<sup>13</sup> thus limiting the number of photons that can be converted into electricity.

One approach to improving DSSCs light harvesting capabilities is the implementation of plasmonics, typically in the form of coinage metal NPs.<sup>14</sup> These plasmonic NPs offer a resonance phenomenon involving the oscillation of the free electron gas in the metal NP, which is driven by the incoming electromagnetic wave. This leads to very strong photon absorption and scattering and to a highly amplified evanescently decaying electromagnetic field at the NP's surface.<sup>15–17</sup> This effect is called localized surface plasmon resonance (LSPR). In DSSCs, the NPs increase the effective absorption cross section by scattering the incoming photons from their path, thus

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enhancing their interaction with the device, and by efficiently coupling the amplified evanescent fields to the semiconductor and the dye.<sup>12</sup>

For solar energy harvesting, visible light (400 to 700 nm) is of interest. AgNPs exhibit a strong LSPR effect in the visible range of the solar spectrum.<sup>18–20</sup> These unique optical properties of AgNPs enhance the light absorption capability of their surrounding environment, with several published examples demonstrating enhanced photocurrents in PV devices owing to AgNP's unique absorptive and scattering capabilities.<sup>18–21</sup>

On the other hand, absorption, and especially LSPR, is a well-known mechanism for energy dissipation in the form of heat that is used, e.g., in biodiagnostics, therapy, and drug delivery.<sup>22</sup> Baffou and Quidant<sup>23</sup> calculated the temperature profile of metal NPs under continuous-wave illumination. They found that the heat density can be greatly nonuniform within an NP. However, at equilibrium, the temperature is generally uniform inside the NP. This behavior is caused by the much larger thermal conductivity of the metal NP in comparison with the (typically nonmetal) surrounding material. The NP's temperature enhancement depends on several parameters (absorption cross section, shape of the NP, thermal conductivity of the surrounding medium, wavelength and irradiance of the incoming light, and distance to the nearest neighboring NPs). For an isolated, spherical (20 nm in diameter:  $\varnothing$ ) AuNP in H<sub>2</sub>O, which is illuminated at a wavelength of 530 nm at an irradiance of 1 mW/ $\mu\text{m}^2$ , a temperature increase of 5°C can be measured. However, when NPs get close to each other, e.g., AuNPs [ $\varnothing$ : (30 ± 3) nm] with distances of (100 ± 10) nm to neighboring NPs, the temperature enhancement can be 100°C (1 mW/ $\mu\text{m}^2$ ,  $\lambda$  = 532 nm).<sup>23,24</sup>

There is a rather large variety of organic dyes that are implemented in DSSCs.<sup>25,26</sup> Ruthenium complex compounds in particular have received high interest as photosensitizers in DSSCs as they show favorable photo-electrochemical properties and a high stability in the oxidized state.<sup>27,28</sup> However, despite these properties, heat damage of ruthenium sensitizers has been reported.<sup>29</sup> Increasing dye degradation temperatures (80°C to 160°C) in DSSCs lead to unfavorable growth of electron recombination rates, decreasing photo-current densities, and drastically reduced open-circuit voltages ( $V_{OC}$ ), all contributing to substantially reduced energy conversion efficiencies ( $\eta$ ).<sup>30</sup>

AgNPs exhibit very similar temperature enhancements compared with AuNPs<sup>31</sup> and are therefore excellent candidates for exploiting the thermostabilizing effect of zirconium-doped TiO<sub>2</sub> as photoactive material in plasmon-enhanced DSSCs. Zirconium (Zr) is one of the most suitable dopants as it is known to have very high thermostabilizing properties. The crystal structures of zirconia and titania are similar enough that Zr<sup>4+</sup> ions can substitute for Ti<sup>4+</sup> ions in the anatase matrix. The resultant ZrO<sub>2</sub> can adopt a tetragonal crystal structure when introduced as a dopant in another tetragonal (e.g., anatase) phase. This is supported by our previously examined density functional theory measurements of ZrO<sub>2</sub> integration into TiO<sub>2</sub>.<sup>32</sup> Maintaining a single phase is beneficial for uninterrupted electron transport during DSSC operation because travelling electrons run a smaller risk of recombination as they do not encounter any grain boundaries, which are common places for traps.

The implementation of Zr-doped TiO<sub>2</sub> NPs (Zr/nTiO<sub>2</sub>) in the photoactive layer of DSSCs has shown a significant influence on the thermal stability of the semiconducting oxide's specific surface area, pore structure, stabilization of the anatase phase, and avoidance of the anatase–rutile phase transition at elevated temperatures, which has consequently enhanced the DSSC performance.<sup>33–37</sup> There are several explanations given for zirconia's thermostabilizing properties on the anatase crystal lattice. For one, Zr<sup>4+</sup> ions are more electropositive than Ti<sup>4+</sup> and are therefore more inclined to donate their electron density to O<sup>2-</sup>. As a result, the neighboring Ti–O bonds in the lattice become more stable and more difficult to break, increasing the lattice's stability at higher temperatures. Zirconia's thermostabilizing properties can also be attributed to its relatively large band gap (~5 eV), making it more of an insulator than TiO<sub>2</sub>. These factors might be of great benefit in mitigating the heat created by LSPR.

Although AgNPs have been shown to amplify absorption in DSSCs, there is a clear limitation of this enhancement due to the creation of heat. For example, Qi et al.<sup>21</sup> observed a decrease in energy conversion efficiency of their fabricated DSSCs when the concentration of AgNPs exceeded 0.6 wt.%. This effect defines an upper limit of the amount of AgNPs that can be incorporated into DSSCs, thus imposing a limit on the cell's absorption improvement. Other

researchers have reported doping limits as well when incorporating plasmonic nanostructures into their photoactive systems, and some simply did not attempt concentrations above 0.5 wt. %.<sup>17,38,39</sup> There are very few studies addressing a moderation by plasmonic-NP doping limits.

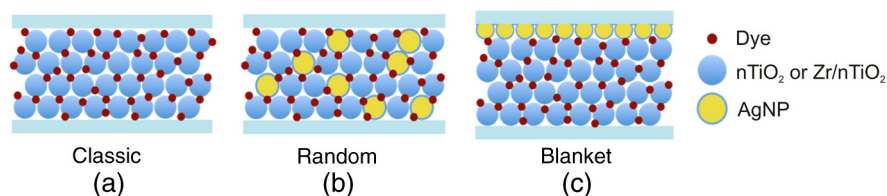
According to several studies,<sup>40,41</sup> a small amount of transition metal doping such as Zr has been found to be very effective in thermally stabilizing TiO<sub>2</sub>. It has one of the highest dielectric constants for metallic oxides<sup>42</sup> and therefore exhibits good optical properties. Additionally, it is very chemically stable due to its multielectronic configuration, including its d-orbital electrons, characteristic of transition metals. Ti and Zr are also in the same group of elements (IVB), which gives them comparable physicochemical properties.

The use of Zr as a thermostabilizer in plasmon-enhanced DSSCs has yet to be investigated, despite the evidence that it increases thermal stability when used as a dopant<sup>43,44</sup> and has been shown to preserve the TiO<sub>2</sub> structure at high temperatures.<sup>45,46</sup> This work examines the effects of incorporating Zr into the nTiO<sub>2</sub> photoactive material in LSPR-enhanced DSSCs, with the goals of stabilizing the nTiO<sub>2</sub> at elevated temperatures (occurring because of plasmonic heating effects), increasing the limit of AgNP concentration in the photoactive layer without provoking negative effects on the cell efficiency, and increasing the overall efficiency in energy conversion.

## 2 Dye-Sensitized Solar Cells Architecture Design

To understand both the role of Zr and the role of the positioning and distribution of AgNPs in DSSC efficiencies, three different cell-architectures were designed (Fig. 1): (a) nTiO<sub>2</sub> or Zr/nTiO<sub>2</sub> as the photoactive material between a standard transparent fluorinated tin oxide (FTO) working electrode (photo-anode) and a Pt counter-electrode as the “classic” architecture without plasmonic features, (b) nTiO<sub>2</sub> or Zr/nTiO<sub>2</sub> as the matrix containing “randomly” mixed nanoaggregates of AgNPs in Zr-free TiO<sub>2</sub> (Ag/nTiO<sub>2</sub>), sandwiched between the two electrodes, and (c) nTiO<sub>2</sub> or Zr/nTiO<sub>2</sub> as the matrix between two electrodes, one of which is the photo-anode carrying a layer of AgNPs covered by a “blanket” of Zr-free TiO<sub>2</sub>. The “italic” expressions are used throughout the paper to name the designs. The random and blanket designs (Fig. 1) offer different strategies (location and density of the AgNPs) for coupling the plasmonics of the AgNPs to the nTiO<sub>2</sub> or Zr/nTiO<sub>2</sub> photoactive semiconductor material and investigating their influence on thermostabilization. The random approach consists of AgNPs (randomly present in a Zr-free nanoagglomerate of nTiO<sub>2</sub>, in Fig. 1 indicated as randomly positioned AgNPs in the photoactive layer) positioned randomly and relatively sparsely throughout the entire photoactive material of the DSSC, whereas the blanket design consists of pure AgNPs immobilized chemically with a relative high density only on top of the photo-anode via poly(4-vinylpyridine) (P4VP). The interaction of the incoming light and the Zr/nTiO<sub>2</sub> with the AgNP is different in both designs. The heat production due to LSPR should also be different.

In the random design, the AgNPs serve both as scattering centers and LSPR field enhancement locations for boosting dye absorption and excitation. Scattering leads to an extension of the interaction length of the incoming light in the photoactive layer, and the amplified evanescent fields around the AgNPs increase the absorption cross section effectively. Since the rate of electron excitation in the dye is proportional to the local light intensity,<sup>47</sup> the LSPR field enhancement encourages the creation of more electron-hole pairs, which should lead to a higher photocurrent and, thus, increased PV efficiency.



**Fig. 1** Schemes of the three DSSC designs. (a) Nonplasmonic AgNP-free nTiO<sub>2</sub> or Zr/nTiO<sub>2</sub> matrix (classic), (b) plasmonic Ag/nTiO<sub>2</sub> aggregate (random) within a nTiO<sub>2</sub> or Zr/nTiO<sub>2</sub> matrix, and (c) plasmonic pure AgNPs as a layer close to the photo anode (coated with a covering blanket of TiO<sub>2</sub>) on a nTiO<sub>2</sub> or Zr/nTiO<sub>2</sub> matrix.

In the random design, the AgNP density in the photoactive material is relatively low; however, it is not homogeneously distributed. Therefore, it is quite possible that some AgNPs are located close to each other within the Ag/nTiO<sub>2</sub> aggregates, creating centers of high-temperature rise in a matrix with mainly low-temperature rise. Mainly small (5°C) to medium (<<100°C) temperature enhancements are expected. Since the Zr/nTiO<sub>2</sub> is close to the aggregated Ag/nTiO<sub>2</sub> material, the Zr/nTiO<sub>2</sub> is also very close to the outermost AgNPs in the individual aggregates but further away from the inner AgNPs in the aggregate. Due to the nanoscopic dimensions of the components of the photoactive material components, and the heat conductivity of the nanoscopic materials and the electrolyte, temperature equilibration between Ag/nTiO<sub>2</sub> aggregates and the Zr-doped material should be quickly achieved.

In the blanket design, the AgNPs mainly serve as scattering centers to extend the interaction length of the photons to be harvested in the photoactive layer.<sup>48</sup> The LSPR field enhancement is not expected to contribute substantially to the dye absorption in the bulk DSSC as most of the dye molecules are too far away. However, when NPs are positioned at the interface between two dielectrics, light will scatter preferentially into the dielectric with the larger permittivity.<sup>48</sup> The permittivity of TiO<sub>2</sub> ( $\epsilon \sim 100$ )<sup>49,50</sup> is higher than that of the polymer (P4VP-10) ( $\epsilon \sim 2.56$ )<sup>51</sup> binding the AgNPs to the electrode. Therefore, the incident light is scattered preferentially into the TiO<sub>2</sub> layer. The scattering cross sections can reach values as high as 10 times the geometrical area.<sup>52,53</sup> The AgNP density above the blanket (Fig. 1) is relatively high and will create locally elevated temperatures. In the blanket design, the Zr/nTiO<sub>2</sub> is relatively far away from the AgNPs and will act on heat mainly due to heat conductivity.

The efficiencies of DSSCs of the three different designs with various AgNP concentrations and Zr concentrations were compared to investigate the influence of the AgNP locations and density and the effect of Zr-thermostabilization.

### 3 Fabrication of Dye-Sensitized Solar Cells

#### 3.1 Materials

The FTO working electrodes, Pt counter-electrodes, polymer gaskets, electrolyte (Iodolyte Z-150), rubber syringes, and polymer sealing were all purchased from Solaronix (Aubonne, Switzerland). N719 dye [cis-Bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II)], terpineol (95%), titanium(IV) isopropoxide (TIP; 97%), and acetylacetone (acac; >99%) were purchased from Sigma-Aldrich (Oakville, Ontario, Canada). Isopropanol (99.5%), acetonitrile-190 (99.8%), *N,N*-dimethylformamide (DMF; 99%), and toluene (99.5%) were purchased from Caledon (Georgetown, Ontario, Canada). Anhydrous ethanol was purchased from Commercial Alcohols (Toronto, Ontario, Canada).

FTO electrodes (thickness, 2.2 mm; sheet resistance, 7 Ω/sq) were purchased from Solaronix (Aubonne, Switzerland). Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%) was purchased from Caledon (Georgetown, Ontario, Canada). Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 wt.% in H<sub>2</sub>O) and poly(4-vinylpyridine) (P4VP, average MW ~ 60,000 D) were purchased from Sigma-Aldrich (Oakville, Ontario, Canada). Sparkleen detergent solution was purchased from Fisher Scientific, Ottawa, Ontario, Canada. Argon was purchased from Praxair, Canada.

Nanosized nTiO<sub>2</sub> (anatase), Zr-doped, nanosized Zr/nTiO<sub>2</sub> (anatase) with 5 and 10 mol.% Zr, and Ag/nTiO<sub>2</sub>, an aggregated, random mixture of AgNPs and nTiO<sub>2</sub> [with 2.5 wt.% Ag in the nTiO<sub>2</sub> (anatase) and AgNP's  $\varnothing < 9$  nm] were synthesized via a modified sol-gel route.<sup>33,54-56</sup> In these aggregates, the AgNPs are only partially sealed with TiO<sub>2</sub>, thus exhibiting some exposed AgNP surfaces. Pure AgNPs were synthesized according to Evanoff and Chumanov.<sup>57</sup>

#### 3.2 Fabrication and Assembly of the Classic and Random Design Dye-Sensitized Solar Cells

2.5- × 2.5-cm fluorine-doped tin oxide (FTO) glass electrodes (thickness: 2.2 mm; sheet resistance: 7 Ω/sq) were first cleaned in Sparkleen detergent solution to remove residual organic

contaminants, followed by deionized water and isopropanol. Between each wash, the electrodes were sonicated for 10 min. The cleaned electrodes were stored in isopropanol and were blown dry using Ar before use. 2- × 2-cm Pt counter-electrodes (thickness: 2 mm) were cleaned in the same manner.

The paste for the photoactive layer was prepared by mixing first powders of nTiO<sub>2</sub> (anatase) or Zr/nTiO<sub>2</sub> (anatase) with or without an appropriate mass of Ag/nTiO<sub>2</sub> (anatase) powder<sup>33,54–56</sup> to obtain 0.3, 0.6, 0.9, 5, 10, 50, and 100 wt.% Ag/nTiO<sub>2</sub> containing (Zr-)titania powder. Thirty milligrams of the resulting titania-based powder was blended with 0.5 ml of a binder solvent (custom made: 20% ethyl cellulose in ethanol, terpineol and acetic acid), and the resulting slurry subsequently was ground in a mortar with a pestle until a homogeneous gluey consistency was achieved. The photoactive layers were formed by doctor blading a film of paste onto a cleaned FTO glass electrode using a tape template of an area of 0.1257 cm<sup>2</sup>, cut with a circular die cutter. The paste was left to dry in air at room temperature for 30 min, then calcined at 500°C for 1 h. The temperature ramp was set to 15°C/min to avoid surface cracking of the film and to ensure proper adhesion to the FTO glass.

After cooling to about 80°C, the photo-electrodes were immersed into a 0.25-mM N719 dye solution containing a 1:1 volume ratio of tert-butanol and acetonitrile and left to immerse for 24 h at room temperature. After dyeing, the sensitized photoanodes were washed with anhydrous ethanol to remove any excess of dye molecules to ensure that the porous nTiO<sub>2</sub> film was covered with a monolayer of dye.

After activating the Pt counter-electrodes by heating them on a hotplate at 120°C for a few minutes, the sensitized photo-anodes and the Pt counter-electrodes were assembled in a sandwich-like configuration and sealed with a hot-melt gasket at 120°C. The electrolyte, which contained 150 mM of the iodide/tri-iodide redox couple, was introduced into the cells through a predrilled hole in the counter electrode using a rubber syringe. The Pt electrodes were purchased with one predrilled hole, but a secondary hole was drilled to facilitate air displacement while filling the cell with the electrolyte. Finally, the holes were sealed with a hot-melt polymer and a cover glass (Zeiss, 0.17-mm thickness) to avoid leakage or evaporation of the electrolyte. All fabrication steps were performed under atmospheric conditions. For statistical purposes, six cells were fabricated for each sample to ensure reproducibility.

### 3.3 Preparation of Blanket Design Photo-Anodes

In the blanket design, pure AgNPs<sup>57</sup> were coated with a thin layer (blanket) of TiO<sub>2</sub> by atomic layer deposition (ALD) with a Savannah 100 Cambridge Nanotech (Waltham, Massachusetts) ALD instrument. The TiO<sub>2</sub> blanket prevented direct contact between the AgNPs and the electrolyte, avoiding the back reaction of electrons to the redox couple during cell operation. ALD was implemented here as the method of choice to protect the pure AgNPs with a layer of TiO<sub>2</sub> because it ensures well-defined, conformal growth of TiO<sub>2</sub>.

To prepare a blanket design electrode, FTO-coated glass electrodes were first cleaned with Piranha solution (3:1 H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>) for 30 min at room temperature. This treatment not only removes all organic contaminants from the FTO surface but also leaves it highly active by introducing hydroxyl groups. Note: this solution reacts violently with most solvents and surfaces, and extreme caution was exercised when carrying out this cleaning step. After the Piranha treatment, the electrodes were thoroughly rinsed with deionized water before being blown dry with Ar gas. The cleaned FTO substrates were functionalized with P4VP by immersing them in an ethanol solution containing 2 wt.% P4VP for 3 h. The electrodes were then rinsed with ethanol to remove any nonadsorbed polymer and heated in an oven for 1 h at 100°C (20°C/min ramp) to relax the monolayer of P4VP, facilitating a homogeneous distribution of the pure AgNPs on the surface. The P4VP-functionalized electrodes were then immersed in the pure AgNP suspension. Having empty d-orbitals characteristic of transition metals, the pure AgNPs in the solution bind strongly to P4VP through the lone pair of electrons on the nitrogen of the pyridine ring. After 12 h of immersion, the AgNP-coated electrodes were rinsed with deionized water and dried with Ar before finally undergoing ALD to create a uniform TiO<sub>2</sub> layer on the AgNPs. To form a pin-hole-free (fully protective, fully covering) TiO<sub>2</sub> layer, 300 cycles of TiO<sub>2</sub> precursor were deposited. Alternating 0.1-s pulses of the precursors TIP and H<sub>2</sub>O were used to form the TiO<sub>2</sub> layer.

A TiO<sub>2</sub> thickness of ~7.7 nm was achieved.<sup>58</sup> The precursors were held in the deposition chamber for 1 s before a 12 s pump. The chamber temperature was set to 200°C, and the N<sub>2</sub> flow rate was 20 sccm. TIP was held at 80°C, and all other precursors were used at room temperature.

After the ALD step, the photoactive paste (see Sec. 3.2) was doctor bladed onto the electrode and the DSSC assembled as described above. For statistical purposes, six cells of each type were fabricated to ensure reproducibility.

## 4 Characterization

### 4.1 General Analysis

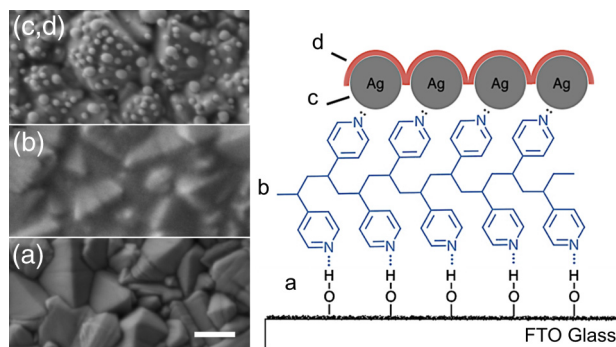
The photo-anodes of the blanket design were characterized with a scanning electron microscope (SEM: LEO-Zeiss 1540 XB, Zeiss, Oberkochen, Germany). A Kratos AXIS ultra x-ray photoelectron spectrometer (XPS) equipped with a monochromatic Al K $\alpha$  x-ray source was used to analyze the surface composition of each layer prepared on the photo-anode of the blanket design.

The LSPR absorption spectra were taken with a Shimadzu UV-3600 UV-vis-NIR spectrometer. The power conversion efficiency of the cells was measured using the simulated illumination of a Newport Oriel 92250A-1000 (Irvine, California) solar simulator and a Keithley 2420 (Cleveland, Ohio) digital source meter.

### 4.2 Characterization of the Blanket Design Dye-Sensitized Solar Cell Photo-Anode

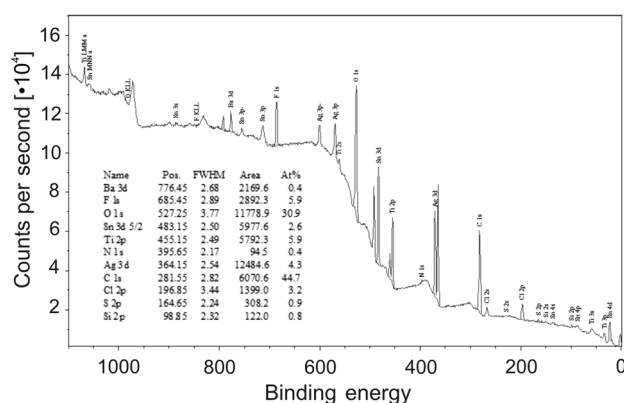
The LSPR peak position ( $\lambda_{\text{max}}$ ) of the pure AgNPs dispersed in water (refractive index of water:  $n = 1.33$ ) was at 430 nm. The LSPR peak position in an environment of TiO<sub>2</sub> with a refractive index of at least 2.45 (for anatase)<sup>59-61</sup> is expected to shift considerably toward the red into the visible.

The layer system comprising the blanket design photo-anode and corresponding SEM images taken throughout the electrode's layer fabrication process is depicted in Fig. 2. Figure 2(a) shows the Piranha treated surface of FTO glass as a polycrystalline, densely agglomerated surface with relatively sharp edged features. The deposition of P4VP smears out the sharp features of the FTO crystallites [Fig. 2(b)]. The deposition of AgNPs and the ALD of TiO<sub>2</sub> leads to indistinguishable SEM images [Figs. 2(c) and 2(d)]. The AgNPs and the TiO<sub>2</sub> layers further smooth the polycrystalline agglomerate structure of the FTO glass electrode and introduce new roundish structures on top of those agglomerates ( $\varnothing$ : 20 to 70 nm), which are interpreted as clustered AgNPs (coated with TiO<sub>2</sub>). The density of the AgNPs is very high and comparable to densities of samples investigated by Baffou et al.,<sup>24</sup> leading to high expected temperature enhancements on the order of 100°C.



**Fig. 2** Scheme of the layer system of the blanket design photo-anode and the corresponding SEM images taken throughout the layer-by-layer fabrication process. (a) Piranha-treated FTO glass; (b) after P4VP-functionalization; (c) and (d) AgNPs bonded to P4VP and TiO<sub>2</sub> layer deposited via ALD. TiO<sub>2</sub>-coated AgNPs are indistinguishable from uncoated AgNPs by SEM. Scale bar in panel “a” (200 nm) applies to all panels.





**Fig. 3** XPS survey spectrum of sample after ALD (300 cycles TiO<sub>2</sub>).

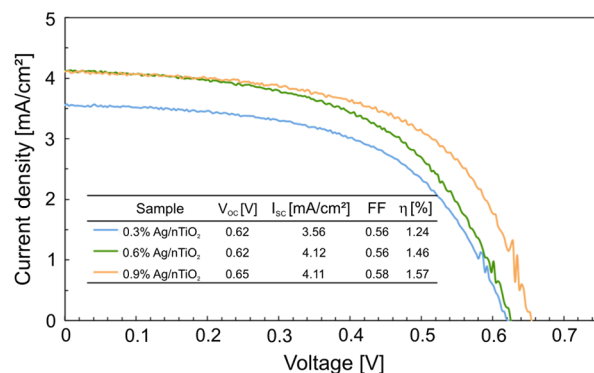
XPS was used to confirm the elemental composition of each layer of the electrode as this technique is well suited to target the top ~10 nm depth of a sample's surface. An XPS survey scan (Fig. 3) confirmed the presence of Ag and Ti in the top two layers of the electrode. The spectra of the AgNPs-coated surface of the electrode revealed that tin, oxygen, carbon, and small amounts of nitrogen were present in the sample. The Ag 3d peak appeared after immersing the P4VP-functionalized slides in the AgNP suspensions. The major XPS peaks for the TiO<sub>2</sub>-coated surface include Ag 3d, Ti 2p, and O 1s. Because 300 cycles of ALD-coated TiO<sub>2</sub> are only ~7.7-nm thick, the spectrometer can still detect the Ag 3d signal, although it was weaker than in the absence of the TiO<sub>2</sub> layer.

## 5 Results and Discussion

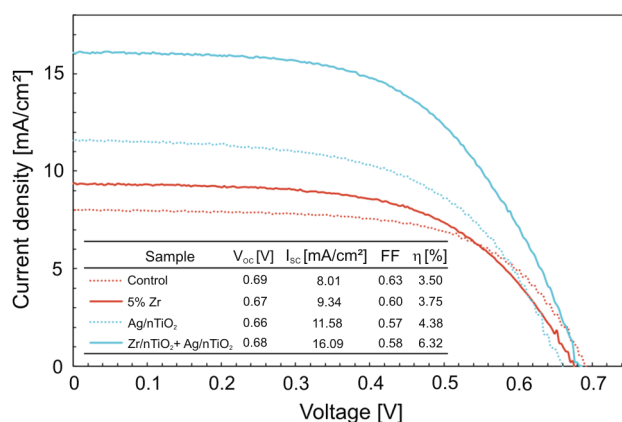
### 5.1 Performance of the Random Design in Dye-Sensitized Solar Cells

First, the energy conversion efficiency ( $\eta$ ) was studied with respect to the concentration of Ag/nTiO<sub>2</sub> present in the Zr/nTiO<sub>2</sub> photoactive material (10% Zr) of the DSSCs. The current density–voltage (I–V) curves of the plasmonic random design DSSCs with 0.3, 0.6, and 0.9 wt. % of Ag/nTiO<sub>2</sub> concentration are shown in Fig. 4. The inset lists the PV characteristics derived from the I–V curves, including the open-circuit voltage ( $V_{OC}$ ), short-circuit current density ( $I_{SC}$ ), fill factor (FF), and energy conversion efficiency.<sup>62</sup>

An enhancement of 18% in energy conversion efficiency ( $\eta = 1.24\% \rightarrow 1.46\%$ ) was found by doubling the Ag/nTiO<sub>2</sub> concentration (0.3 wt.%  $\rightarrow$  0.6 wt.%). Tripling the concentration to 0.9 wt.% resulted in another 9% increase in efficiency ( $\eta = 1.57\%$ ). Even though the AgNPs



**Fig. 4** Current density–voltage curves for DSSCs fabricated with a matrix of 10 mol.% Zr/nTiO<sub>2</sub> containing various concentrations Ag/nTiO<sub>2</sub>. The inset shows the DSSC's characteristics calculated from the I–V curves.



**Fig. 5** The effect of Zr/nTiO<sub>2</sub> on Ag/nTiO<sub>2</sub> containing DSSCs. Measured I–V curves for the classic and random designed DSSCs in comparison with a control sample (nTiO<sub>2</sub>). The inset shows the characteristic data calculated from the I–V curves.

were partly unprotected, doubling the Ag/nTiO<sub>2</sub> concentration increased the photocurrent, a sign of increased carrier extraction. These results imply that the unprotected AgNPs surface in the aggregates was low enough that the benefits from the LSPR outweighed the disadvantage from the exposed AgNP surface, acting as recombination sites for electrons.<sup>63,64</sup>

Tripling the Ag/nTiO<sub>2</sub> concentration to 0.9 wt.% also showed an improvement in the V<sub>OC</sub>, but the I<sub>SC</sub> began to fall. The higher V<sub>OC</sub> was expected and reveals that the AgNPs were indeed acting mainly via their LSPR field enhancement as light absorption boosters, generating more efficient electron-hole separation. However, the lack of improvement in the I<sub>SC</sub> is an indication that the extra charge carriers being created were not extracted efficiently into the external circuit, but rather were recombining or quenched, probably at exposed AgNP surfaces.<sup>65</sup> At 0.9 wt.% Ag/nTiO<sub>2</sub>, the overall unprotected surface area of AgNPs in the photoactive material exceeded a critical value at which undesired electron recombination compensates for the advantageous plasmonic assistance.

Further enhancement of the Ag/nTiO<sub>2</sub> concentration (I–V data not shown) led to a maximum in η of 1.85% (at 5 wt.%) but to a substantial drop from η = 1.74% (at 50 wt.%) to η = 0.69% (at 100 wt.%). Despite the increasing electron recombination at the unprotected AgNP surfaces, the amount of AgNPs in the photoactive material could be enhanced to 50 wt.% of Ag/nTiO<sub>2</sub>, translating to a AgNP content of 1.25 wt.% within the photoactive material, a value twice as high as the AgNP content of Qi et al.<sup>21</sup> The main difference between this DSSC system (in addition to the incomplete shielding of the AgNPs from the electrolyte) and Qi's devices is the presence of Zr in the nTiO<sub>2</sub> crystals. The AgNPs are mainly dispersed and should raise the temperature in the photoactive material moderately. However, with increasing AgNP concentration, larger AgNP clusters are more likely to form, therefore increasing the likelihood of higher temperatures within the layer. The Zr-doping substantially prevented heat damage, which limited the energy conversion efficiency, at least up to 50 wt.% of Ag/nTiO<sub>2</sub>.

In Fig. 5, the I–V curve and the PV data for a control sample fabricated with pure nTiO<sub>2</sub> as the photoactive material are shown (dotted red line). The efficiency in energy conversion for the non-plasmonic, non-Zr-doped case, at η = 3.50%, is substantially higher than in the cases using Ag/nTiO<sub>2</sub> and Zr/nTiO<sub>2</sub> (10% Zr). This is important information. The nonperfect shielding of the AgNPs from the electrolyte has a destructive impact on η, despite the efficiency stabilization by Zr. It is therefore necessary in the future to take advantage of both the LSPR and the Zr-doping and apply fully protected AgNPs, e.g., as described by Qi et al.<sup>21</sup> in the form of Ag-core/TiO<sub>2</sub> shell NPs.

After determining an “optimum” Ag/nTiO<sub>2</sub> concentration, detailed effects of the Zr-doping on thermal stabilization were tested. Figure 5 relates the efficiency of energy conversion of four different DSSCs: the classic and the random types, fabricated with pure nTiO<sub>2</sub> (control: classic design, no plasmonics), the Zr/nTiO<sub>2</sub> (5% Zr: classic design, no plasmonics), the Ag/nTiO<sub>2</sub> in nTiO<sub>2</sub> (Ag/nTiO<sub>2</sub>: random design, plasmonic), and the Ag/nTiO<sub>2</sub> in

Zr/nTiO<sub>2</sub> (Zr/nTiO<sub>2</sub> + Ag/nTiO<sub>2</sub>: random design, plasmonic). The Ag/nTiO<sub>2</sub> concentration was kept at 0.6 wt.% (the “optimum”) in both DSSC types containing Ag/nTiO<sub>2</sub>. The Zr/nTiO<sub>2</sub> contained 5 mol.% Zr.<sup>33</sup>

The energy conversion efficiency (Fig. 5, inset) systematically increases from the control ( $\eta = 3.50\%$ ), to Zr-doping ( $\eta = 3.75\%$ ),<sup>33</sup> to applying Ag/nTiO<sub>2</sub> ( $\eta = 4.38\%$ ), and finally to  $\eta = 6.32\%$  by applying both Ag/nTiO<sub>2</sub> and Zr/nTiO<sub>2</sub>, representing an overall increase of 81% in efficiency from the control. Roughly half of this increase is obtained with the two plasmonic cases by adding the Zr-doped TiO<sub>2</sub> to Ag/nTiO<sub>2</sub>. This significant enlargement of  $\eta$  is reflected by  $I_{SC}$  values (Fig. 5, inset), which increase parallel to  $\eta$ . An increase in energy conversion efficiency of 7% is found by adding Zr as a thermostabilizer to the classic design.<sup>33</sup>

Limiting the AgNP concentration to 0.6 wt.% Ag/nTiO<sub>2</sub> (which translates to 0.015% Ag in the entire photoactive material) should prevent too many AgNPs in close proximity to each other and, therefore, limit the temperature rise. However, the photoactive material is not homogeneous with respect to the AgNP distribution as they are embedded within the aggregates of the Ag/nTiO<sub>2</sub>. Therefore, some AgNPs, which are close to each other, will produce high temperatures. However, these heat contribution effects are compensated for by Zr-doping.

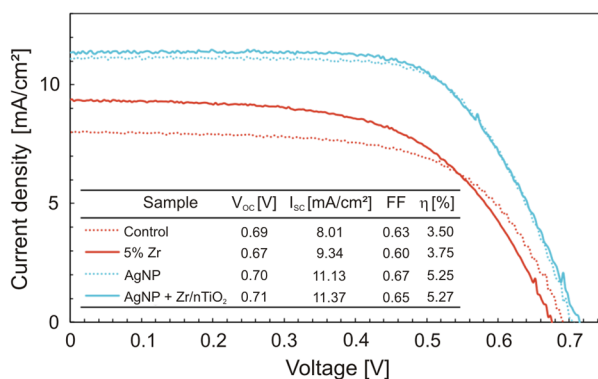
The FF values of the random design cells with plasmonics (blue) were lower than those of the AgNP-free cells (red), an outcome that reflects a decreased charge transport within the cell. As mentioned above, energy conversion efficiencies would have been even higher if the AgNPs’ surfaces in Ag/nTiO<sub>2</sub> would have not been exposed to the electrolyte during cell operation and allowed for some electron recombination at the “optimum” concentration.

## 5.2 Performance of Blanket Design in Dye-Sensitized Solar Cells

In Fig. 6, the current–voltage data of blanket design DSSCs containing AgNPs are compared with the blanket design DSSCs without AgNPs. In addition, two non-plasmonic devices, a control and a Zr-containing classic DSSC, are shown. This figure also stresses the influence on the performance when Zr was incorporated into the photoactive layers of DSSCs provided with a AgNP layer. Note: the Zr-concentration was fixed at 5 mol.% Zr in the nTiO<sub>2</sub>.<sup>33</sup>

First, the data demonstrate that both plasmonic DSSCs (blue) have a higher  $\eta$  than the non-plasmonic devices (red). In addition, and as already discussed for the random design DSSCs, doping the nonplasmonic devices with Zr enhanced the efficiency in energy conversion compared with the control.

Moreover, the introduction of the AgNP layer resulted in an  $\eta$ -enhancement of 50% ( $\eta = 3.50\% \rightarrow 5.25\%$ ), and the addition of Zr/nTiO<sub>2</sub> further led to an additional—but very small—increase in  $\eta$  to 5.27%. The increase due to the pure AgNP layer in DSSCs containing Zr is similar to DSSCs containing no Zr: an enhancement of 40% was found (from  $\eta = 3.75\% \rightarrow 5.27\%$ ). The overall  $\eta$ -enhancement from a control DSSC to the Zr-containing plasmonic device is 51%.



**Fig. 6** The effect of Zr and AgNP doping on the I–V curves of the blanket design DSSCs in comparison with a control sample of nTiO<sub>2</sub>. The inset shows the characteristic data calculated from the I–V curves.

The increase in the efficiency of energy conversion is directly correlated to an increase in photocurrent (Fig. 6 inset), which corresponds to an enhanced light absorption of the dye. The AgNPs on the photo-anode in the blanket design served mainly as a layer of scattering centers to divert the incoming photons and extend the optical path within the cell, thus enhancing the photon interaction and the absorption cross section within the photoactive cell layer compared with the AgNP-free DSSCs. In short, the dye molecules were reached by photons more often, yet no dye molecules were located close to the AgNPs in the blanket cases. The addition of the Zr/nTiO<sub>2</sub>, however, did not improve the cell efficiency substantially. The presence of Zr in the photoactive layer (bulk) had no positive effect on the high heat development expected for the relatively closely-packed AgNPs in the AgNP layer as the Zr/nTiO<sub>2</sub> material was “too far away,” with the thickness of the ALD TiO<sub>2</sub> layer separating them by at least ~7.7 nm. Therefore, thermostabilization only occurred efficiently in the nonplasmonic part of the cell.

### 5.3 Comparison between Designs

In the following, the performance of the photoactive cell layer designs, random and blanket, is compared in detail to determine the important performance characteristics and design factors for an optimized cell design when implementing Zr/nTiO<sub>2</sub> as thermostabilizers in plasmonic DSSCs. First, in contrast to the plasmonic random design cells, higher FF values were observed in the blanket design cells and in the nonplasmonic cells (Figs. 4 and 6, insets). The lower FF values (FF: indicator of electron transport within cells) for cells containing Ag/nTiO<sub>2</sub> are caused by exposed AgNP surfaces, which acted as recombination centers for electrons, preventing them from reaching the exterior circuit. This problem did not appear in the blanket design cells. Thus, it is critical to incorporate AgNPs whose surfaces are completely shielded from contact with the electrolyte.

Table 1 provides an overview of all cell designs with respect to Zr and AgNP incorporation.

In the absence of AgNPs, the incorporation of Zr/nTiO<sub>2</sub> improved the energy conversion efficiency by 7%. This has been found previously due to stabilization of the anatase crystal structure and an increase in the surface area of the nTiO<sub>2</sub> material.<sup>33</sup> From the two AgNP-containing cell architectures, the blanket design achieved the higher efficiency ( $\eta = 5.25\%$ ) if Zr/nTiO<sub>2</sub> was absent. However, this does not contribute to better cell design as the AgNP surfaces in the Ag/nTiO<sub>2</sub> material are partially exposed to electrolyte and, therefore, cause the random design to suffer from increased electron recombination. Despite this shortcoming of the Ag/nTiO<sub>2</sub> material (which can easily be overcome by core-shell AgNPs<sup>21</sup>), the performance of the random design cell surpassed that of the blanket design cell when Zr/nTiO<sub>2</sub> was used as the photoactive layer. Energy conversion efficiencies of  $\eta = 4.38\%$  and  $\eta = 6.32\%$  were achieved by the random design cells and can be improved substantially by a proper AgNP coating strategy.<sup>66</sup> Nonetheless, a clear improvement in efficiency is seen with the inclusion of Zr/nTiO<sub>2</sub>, indicating that the addition of Zr helped to provide enhanced thermal stability. The inclusion of Zr in the blanket cell design did not increase  $\eta$  considerably (see discussion above).

Zr/nTiO<sub>2</sub>'s ability to thermostabilize the DSSC design only functions when the AgNPs are dispersed throughout the photoactive Zr/nTiO<sub>2</sub> matrix, as provided in the random design. However, only small to medium concentrations are desired for well-functional cells as the

**Table 1** Energy conversion efficiencies with respect to cell design and material application.

Cell types	Control	Zr/nTiO <sub>2</sub>	AgNP containing DSSCs		AgNP and Zr/nTiO <sub>2</sub> containing DSSCs	
nTiO <sub>2</sub> (mol.%)	100	95	100	100	95	95
Zr (mol.%)	—	5	—	—	5	5
Design	Classic	Classic	Random	Blanket	Random	Blanket
$\eta$ (%)	3.50	3.75	4.38	5.25	6.32	5.27
$\Delta\eta$ (%)	0	7	25	50	80	51

plasmonic thermal behavior creates minor to severe threats with respect to the collapse of the nTiO<sub>2</sub> matrix, which in turn reduces the surface area and consequently the photo-absorption capabilities of the cell.

Zr exhibited thermostabilization in both AgNP-containing cell designs, but it was more effective in the random design. The drawback of the blanket design is that the enhanced local field from the LSPR only enhanced charge separation for a very limited number of dye molecules located very close to the AgNPs below the “blanket,” finally leading to only a limited photocurrent enhancement. The enhanced photocurrent observed in the blanket design cells, thus, in contrast to the control, can be mainly attributed to plasmonic scattering (where AgNPs acted as scattering centers), enhancing the interaction of the incoming light with the photoactive layer and the dye molecules. Therefore, the random design is the superior cell design for incorporating AgNPs in combination with Zr/nTiO<sub>2</sub> photoactive material in DSSCs.

## 6 Conclusions

The use of Zr/nTiO<sub>2</sub> as a thermostabilizing material in the photoactive layer of DSSCs was investigated for stabilizing nTiO<sub>2</sub> when jeopardized by the plasmonic heat generation created from the presence of AgNPs, whose purpose served to enhance the energy conversion efficiency of the cells. In both cell architectures, the AgNPs were used as field enhancers and scattering centers to more efficiently excite the dye molecules.

The results showed that Zr exhibited thermostabilizing properties in both plasmonic cell architectures. The random design, consisting of AgNPs dispersed throughout the photoactive layer, demonstrated superior performance over the blanket design in the presence of Zr/nTiO<sub>2</sub>. Both the photocurrent and FF were significantly enhanced, and an energy conversion efficiency increase of 44% was observed in the random design when incorporating Zr into the nTiO<sub>2</sub> photoactive matrix. The DSSC's performance can be additionally enhanced via an appropriate coating to avoid electron recombination. This should also lead to individual AgNPs, which can be easier and more evenly dispersed throughout the photoactive layer than the aggregated Ag/nTiO<sub>2</sub> material. Zr did not play a significant role in improving the energy conversion efficiency of blanket design DSSCs as its thermostabilizing benefits were limited in this architecture.

It can be concluded that the random design is the better cell design for a combined incorporation of AgNPs and Zr/nTiO<sub>2</sub> into DSSCs. It also can be concluded that the random design is the overall best alternative for LSPR-enhanced DSSCs. This design allows for both plasmonic features—scattering and field enhancement—to each contribute optimally to the energy conversion efficiency. Therefore, it is important to investigate the threshold concentration of AgNPs in a Zr-doped TiO<sub>2</sub> matrix at which the enhancing plasmonic features are overtaken by disadvantages from too many AgNPs.

It should also be recognized that Zr has a more pronounced positive effect as a thermostabilizing dopant in nTiO<sub>2</sub> for DSSCs when present at elevated calcination temperatures. This is relevant because many processing techniques in industry (not only in PV applications) necessitate temperatures above 500°C. If a material can be processed at low temperatures, then Zr-doping may not be necessary. If, however, low-temperature processing is not an option and elevated temperatures are required (or generated in the case of using plasmonics), results show that adding Zr proves beneficial over the absence of Zr. This could apply to emerging roll-to-roll fabrication processes of flexible DSSCs with thermal or UV-curing where hot spots may occur, where the addition of Zr would help prevent thermal degradation and improve efficiencies. Zr's thermostabilizing effect in plasmon-enhanced DSSCs can therefore lead to new solar cell designs with smaller semiconductor thicknesses and, thus, lower material costs and quicker investment amortization.

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## References

1. J. Wu et al., "Electrolytes in dye-sensitized solar cells," *Chem. Rev.* **115**(5), 2136–2173 (2015).
2. A. Fakharuddin et al., "Perspective on the production of dye-sensitized solar modules," *Energy Environ. Sci.* **7**, 3952–3981 (2014).
3. A. Kojima et al., "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells," *J. Am. Chem. Soc.* **131**(17), 6050–6051 (2009).
4. J.-H. Im et al., "6.5% efficient perovskite quantum-dot-sensitized solar cell," *Nanoscale* **3**, 4088–4093 (2011).
5. H. Hu et al., "Photo-assisted deposition of Ag nanoparticles on branched TiO<sub>2</sub> nanorod arrays for dye-sensitized solar cells with enhanced efficiency," *J. Alloys Compd.* **694**, 653–661 (2017).
6. M. J. Yun et al., "Highly flexible dye-sensitized solar cells produced by sewing textile electrodes on cloth," *Sci. Rep.* **4**, 5322 (2014).
7. W.-Q. Wu et al., "A tri-layered photoanode of TiO<sub>2</sub> nanoparticles on 1D–3D nanostructured TiO<sub>2</sub>—grown flexible Ti substrate for high-efficiency (9.1%) dye-sensitized solar cells with unprecedentedly high photocurrent density," *J. Phys. Chem. C* **118**(30), 16426–16432 (2014).
8. L. Ming et al., "Selective laser sintering of TiO<sub>2</sub> nanoparticle film on plastic conductive substrate for highly efficient flexible dye-sensitized solar cell application," *J. Mater. Chem. A* **2**(13), 4566–4573 (2014).
9. T. Yamaguchi et al., "Highly efficient plastic-substrate dye-sensitized solar cells with validated conversion efficiency of 7.6%," *Sol. Energy Mater. Sol. Cells* **94**(5), 812–816 (2010).
10. M. Eslamian, "Spray-on thin film PV solar cells: advances, potentials and challenges," *Coatings* **4**(1), 60–84 (2014).
11. A. Hagfeldt et al., "Dye-sensitized solar cells," *Chem. Rev.* **110**(11), 6595–6663 (2010).
12. H. A. Atwater and A. Polman, "Plasmonics for improved photovoltaic devices," *Nat. Mater.* **9**, 205–213 (2010).
13. C. Chen et al., "Highly efficient light-harvesting ruthenium sensitizer for thin-film dye-sensitized solar cells," *ACS Nano* **3**(10), 3103–3109 (2009).
14. P. Mandal and S. Sharma, "Progress in plasmonic solar cell efficiency improvement: a status review," *Renewable Sustainable Energy Rev.* **65**, 537–552 (2016).
15. T. Jensen et al., "Electrodynamics of noble metal nanoparticles and nanoparticle clusters," *J. Cluster Sci.* **10**(2) 295–317 (1999).
16. S. K. Cushing and N. Wu, "Plasmon-enhanced solar energy harvesting," *Electrochem. Soc. Interface* **22**, 63–67 (2013).
17. S. Linic, P. Christopher, and D. B. Ingram, "Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy," *Nat. Mater.* **10**, 911–921 (2011).
18. Q. Xu et al., "Plasmonic core-shell metal-organic nanoparticles enhanced dye-sensitized solar cells," *Opt. Express* **20**(S6), A898–A907 (2012).
19. Q. Xu et al., "Broadband light absorption enhancement in dye-sensitized solar cells with Au-Ag alloy popcorn nanoparticles," *Sci. Rep.* **3**, 2112 (2013).
20. X. Dang et al., "Tunable localized surface plasmon-enabled broadband light-harvesting enhancement for high-efficiency panchromatic dye-sensitized solar cells," *Nano Lett.* **13**(2), 637–642 (2013).
21. J. Qi et al. "Highly efficient plasmon-enhanced dye-sensitized solar cells through metal@oxide core-shell nanostructure," *ACS Nano* **5**(9), 7108–7116 (2011).
22. L. A. Austin et al., "The optical, photothermal, and facile surface chemical properties of gold and silver nanoparticles in biodiagnostics, therapy, and drug delivery," *Arch. Toxicol.* **88**(7), 1391–1417 (2014).
23. G. Baffou and R. Quidant, "Thermo-plasmonics: using metallic nanostructures as nano-sources of heat," *Laser Photonics Rev.* **7**(2), 171–187 (2013).
24. G. Baffou et al., "Thermal imaging of nanostructures by quantitative optical phase analysis," *ACS Nano* **6**(3), 2452–2458 (2012).

25. I. N. Obotowo, I. B. Obot, and U. J. Ekpe, "Organic sensitizers for dye-sensitized solar cell (DSSC): properties from computation, progress and future perspectives," *J. Mol. Struct.* **1122**, 80–87 (2016).
26. K. Hara and N. Koumura, "Organic dyes for efficient and stable dye-sensitized solar cells," *Mater. Matters* **4**(4), 92–98 (2009).
27. Y. Qin and Q. Peng, "Ruthenium sensitizers and their applications in dye-sensitized solar cells," *Int. J. Photoenergy* **2012**, 1–21 (2012).
28. O. Kohle et al., "The photovoltaic stability of, bis(isothiocyanato)ruthenium(II)-bis-2, 2'-bipyridine-4, 4'-dicarboxylic acid and related sensitizers," *Adv. Mater.* **9**(11), 904–906 (1997).
29. S. Hassing et al., "Investigation of the stability of the ruthenium-based dye (N719) utilizing the polarization properties of dispersive Raman modes and/or of the fluorescent emission," *J. Phys. Chem. C* **117**(45), 23500–23506 (2013).
30. S. Sarker, H. W. Seo, and D. M. Kim, "Electrochemical impedance spectroscopy of dye-sensitized solar cells with thermally degraded N719 loaded TiO<sub>2</sub>," *Chem. Phys. Lett.* **585**, 193–197 (2013).
31. A. P. Bell et al., "Quantitative study of the photothermal properties of metallic nanowire networks," *ACS Nano* **9**(5), 5551–5558 (2015).
32. R. A. Lucky et al., "Effect of solvent on the crystal growth of one-dimensional ZrO<sub>2</sub>-TiO<sub>2</sub> nanostructures," *Cryst. Growth Des.* **10**(4), 1598–1604 (2010).
33. A. Pasche et al., "Zr-doped TiO<sub>2</sub> nanoparticles synthesized via a sol-gel route and their application in dye-sensitized solar cells for thermo-stabilization," *Mater. Res. Express* **4**, 065501 (2017).
34. M. Dürr et al., "Band-gap engineering of metal oxides for dye-sensitized solar cells," *J. Phys. Chem. B* **110**(43), 21899–21902 (2006).
35. A. Kitiyanan et al., "Structural and photovoltaic properties of binary TiO<sub>2</sub> – ZrO<sub>2</sub> oxides system prepared by sol-gel method," *Compos. Sci. Technol.* **66**, 1259–1265 (2006).
36. M. D. Hernández-Alonso et al., "Sol-gel preparation of TiO<sub>2</sub> – ZrO<sub>2</sub> thin films supported on glass rings: influence of phase composition on photocatalytic activity," *Thin Solid Films* **502**(1–2), 125–131 (2006).
37. D. J. Reidy, J. D. Holmes, and M. A. Morris, "Preparation of a highly thermally stable titania anatase phase by addition of mixed zirconia and silica dopants," *Ceram. Int.* **32**, 235–239 (2006).
38. B. Paci et al., "Enhancement of photo/thermal stability of organic bulk heterojunction photovoltaic devices via gold nanoparticles doping of the active layer," *Nanoscale* **4**, 7452–7459 (2012).
39. S. Link and M. A. El-Sayed, "Size and temperature dependence of the plasmon absorption of colloidal gold nanoparticles," *J. Phys. Chem. B* **103**(21), 4212–4217 (1999).
40. R. A. Lucky and P. A. Charpentier, "A one-step approach to the synthesis of ZrO<sub>2</sub>-modified TiO<sub>2</sub> nanotubes in supercritical carbon dioxide," *Adv. Mater.* **20**(9), 1755–1759 (2008).
41. R. A. Lucky, Y. Medina-Gonzalez, and P. A. Charpentier, "Zr doping on one-dimensional titania nanomaterials synthesized in supercritical carbon dioxide," *Langmuir* **26**(24), 19014–19021 (2010).
42. A. Sashchiuk et al., "Optical and conductivity properties of PbS nanocrystals in amorphous zirconia sol-gel films," *J. Sol-Gel Sci. Technol.* **24**, 31–38 (2002).
43. Z. Miao et al., "One-pot synthesis of ordered mesoporous zirconium oxophosphate with high thermostability and acidic properties," *Catal. Sci. Technol.* **3**, 1942–1954 (2013).
44. B. Djuricic et al., "Thermal stability of transition phases in zirconia-doped alumina," *J. Mater. Sci.* **32**, 589–601 (1997).
45. S. Chang and R. Doong, "Characterization of Zr-doped TiO<sub>2</sub> nanocrystals prepared by a nonhydrolytic sol-gel method at high temperatures," *J. Phys. Chem. B* **110**, 20808–20814 (2006).
46. E. Kraveva et al., "Phase formation in mixed TiO<sub>2</sub> – ZrO<sub>2</sub> oxides prepared by sol-gel method," *J. Struct. Chem.* **52**, 330–339 (2011).
47. M. K. Kumar et al., "Field effects in plasmonic photocatalyst by precise SiO<sub>2</sub> thickness control using atomic layer deposition," *ACS Catal.* **1**(4), 300–308 (2011).

48. J. Mertz, "Radiative absorption, fluorescence, and scattering of a classical dipole near a lossless interface: a unified description," *J. Opt. Soc. Am. B* **17**(11), 1906–1913 (2000).
49. S. Marinell et al., "Broadband dielectric characterization of TiO<sub>2</sub> ceramics sintered through microwave and conventional processes," *Ceram. Int.* **39**, 299–306 (2013).
50. Z. Ahmad, "Polymeric dielectric materials," Chapter 1 in *Engineering, Electrical and Electronic Engineering, Dielectric Media*, M. A. Silaghi, Ed., InTech (2012).
51. S. Scheinert et al., "Low-cost submicrometer organic field-effect transistors," Chapter 6 in *Advances in Polymer Sciences, Organic Electronics*, T. Grasser, G. Meller, and L. Li, Eds., Vol. **223**, pp. 155–188, Springer, Berlin, Heidelberg (2010).
52. K. R. Catchpole and A. Polman, "Design principles for particle plasmon enhanced solar cells," *Appl. Phys. Lett.* **93**(19), 191113 (2008).
53. C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, Wiley, New York (1983).
54. A. Pasche, "Doping plasmon-enhanced TiO<sub>2</sub> with zirconia to improve solar energy harvesting in dye-sensitized solar cells," Master Thesis, University of Western Ontario, Canada (2015).
55. Y. Chen et al., "Microstructure and properties of polyester-based polyurethane/titania hybrid films prepared by sol-gel process," *Polymer* **47**(5), 1640–1648 (2006).
56. R. Sui and P. A. Charpentier, "Synthesis of metal oxide nanostructures by direct sol-gel chemistry in supercritical fluids," *Chem. Rev.* **112**(6), 3057–3082 (2012).
57. D. D. Evanoff and G. Chumanov, "Size-controlled synthesis of nanoparticles. 1. 'Silver Only' aqueous suspension via hydrogen reduction," *J. Phys. Chem. B* **108**(37), 13948–13956 (2004).
58. S. D. Standridge, G. C. Schatz, and J. T. Hupp, "Toward plasmonic solar cells: protection of silver nanoparticles via atomic layer deposition of TiO<sub>2</sub>," *Langmuir* **25**(5), 2596–2600 (2009).
59. J. G. Liu et al., "Optically transparent sulfur-containing polyimide-TiO<sub>2</sub> nanocomposite films with high refractive index and negative pattern formation from poly(amic acid)-TiO<sub>2</sub> nanocomposite film," *Chem. Mater.* **20**(1), 273–281 (2008).
60. A. Herman et al., "Controlling the crystallinity and nonlinear optical properties of transparent TiO<sub>2</sub>-PMMA nanohybrids," *J. Mater. Chem.* **14**, 2978–2987 (2004).
61. H. Tang et al., "Optical properties of anatase (TiO<sub>2</sub>)," *Solid State Commun.* **92**(3), 267–271 (1994).
62. J. A. Mazer, *Solar Cells: An Introduction to Crystalline Photovoltaic Technology*, Kluwer Academic Publishers, Boston, Massachusetts (1997).
63. L. M. Santos et al., "Structural characterization of Ag-doped TiO<sub>2</sub> with enhanced photocatalytic activity," *RSC Adv.* **5**(125), 103752–103759 (2015).
64. Y. Huang et al., "Preparation of nitrogen-doped TiO<sub>2</sub> nanoparticle catalyst and its catalytic activity under visible light," *Chin. J. Chem. Eng.* **15**(6), 802–807 (2007).
65. C. T. Yip et al., "Strong competition between electromagnetic enhancement and surface-energy-transfer induced quenching in plasmonic dye-sensitized solar cells: a generic yet controllable effect," *Nano Energy* **26**, 297–304 (2016).
66. R. T. Tom et al., "Freely dispersible Au@TiO<sub>2</sub>, Au@ZrO<sub>2</sub>, Ag@TiO<sub>2</sub>, and Ag@ZrO<sub>2</sub> core-shell nanoparticles: one-step synthesis, characterization, spectroscopy, and optical limiting properties," *Langmuir* **19**(8), 3439–3445 (2003).

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