Review

Light trapping and plasmonic enhancement in silicon, dye-sensitized and titania solar cells

Hong Nhung Tran\textsuperscript{1,2}, Van Hieu Nguyen\textsuperscript{1,2}, Bich Ha Nguyen\textsuperscript{1,2} and Dinh Lam Vu\textsuperscript{1}

\textsuperscript{1} Institute of Materials Science and Advanced Center of Physics, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet, Cau Giay, Hanoi, Vietnam
\textsuperscript{2} University of Engineering and Technology, Vietnam National University, 144 Xuan Thuy, Cau Giay, Hanoi, Vietnam

E-mail: thnhung@iop.vast.ac.vn

Received 31 August 2015
Accepted for publication 4 November 2015
Published 8 January 2016

Abstract

The efficiency of a solar cell depends on both the quality of its semiconductor active layer, as well as on the presence of other dielectric and metallic structural components which improve light trapping and exploit plasmonic enhancement. The purpose of this work is to review the results of recent research on light trapping and plasmonic enhancement in three types of solar cells: thin-film silicon solar cells, dye-sensitized solar cells and solid-state titania solar cells. The results of a study on modeling and the design of light trapping components in solar cells are also presented.

Keywords: solar cell, light trapping, plasmonic enhancement, silicon, dye-sensitized, titania

Classification numbers: 2.01, 2.09, 4.02, 5.04

1. Introduction

The efficiency of a solar cell depends not only on the ability of active semiconducting materials to absorb the sunlight and convert solar energy into a photocurrent or photovoltage, but also on the appropriate design of the solar cell, such that sunlight is perfectly trapped in the layer of its active semiconducting material. This problem was intensively studied in a series of experimental (and computational) works by Atwater, Polman \textit{et al} [1–11] on plasmonic light trapping in thin-film Si solar cells, and the obtained results were presented in a review [12]. The content of this review comprised three parts. In the first part, the authors presented their systematic study of plasmon-mediated light coupling in a substrate with metal nanostructures placed at the front of the solar cell, and investigated the effect of particle shape, size and array pitch on the coupling of light, using both simulation and experiments. Total reflectance spectroscopy carried out on a thick crystalline Si(c-Si) solar cell showed that optimized plasmonic antireflection (AR) coatings can be better than standard planar dielectric coatings. In the second part, the authors analyzed the coupling of light to guided optical modes in a thin semiconductor layer. A silicon-on-insulator (SOI) wafer with a 200 nm c-Si region was used as a model system for solar cells to investigate the mechanism of light coupling to waveguide modes in ultrathin optically active layers. The coupling to waveguide modes was studied theoretically, using a transfer matrix method, and experimentally, using the photoluminescence of $E_{1s}^{\text{val}}$ ions in the waveguide as a trapped light intensity probe. In the third part, the authors demonstrated the integration of plasmonic nanostructures into...
showed enhanced efficiency using an inexpensive and scalable nanoimprint process and experiments and simulation. The patterns were fabricated on top of the cell, and by angular distribution of the scattered light, and light trapping by light coupling to photonic modes of the semiconductor due to corrugation in the metal back surface.

The purpose of the present article is to review the results of several interesting works which were not included in the review [12]. These include advances in the study of plasmonic light trapping in thin-film Si solar cells achieved after the submission of the review [12], research progress on dye-sensitized solar cells (DSSCs), and the results of pioneering experimental work on solid-state titania-based solar cells with plasmonic enhancement—the plasmonic titania solar cells.

The content of section 2 covers the basics of light trapping in silicon solar cells, as well as their modeling and design. A review on plasmonic enhancement in silicon solar cells is presented in section 3. In section 4 we summarize the results of selected experimental works on plasmonic enhancement in dye-sensitized solar cells (DSSCs). Section 5 is devoted to a review of research on plasmonic titania solar cells. The conclusion and discussions are presented in section 6.

2. Basics of light trapping in silicon solar cells, their modeling and design

Plasmonic solar cells usually have sophisticated structures which require careful modeling and design. The typical modeling for plasmonic hydrogenated amorphous silicon (a-Si:H) solar cells was elaborated by Atwater et al [13]. Ultrathin absorbing layers are particularly important for a-Si:H solar cells for reasons of long-term stability and manufacturing through-put. The authors used the conformal nature of deposition to form each integrated device with both plasmonic back-contact light trapping and photonic front-surface light trapping. Through a combination of local and guided mode resonances, the broadband response was predicted and the roles of the different interfaces were explored.

Optical models took into account the geometry of the system, as well as the optical properties of all the materials—so it was important to model each of these elements accurately. Given realistic cell depositions, the actual shape of the fabricated device is critical. The authors performed electromagnetic modeling and optimization of the solar cells using experimental cross sections and atomic force microscopy (AFM) data as a guide to modeling realistic cell architectures and applying the finite difference time domain (FDTD) method. All modeling of the necessary spacer layers and optically relevant contacts was included. The modeled solar cell consisted of a patterned metal back-contact with 100 nm tall hemi-ellipsoidal Ag particles on a continuous Ag film, a 130 nm thick layer of ZnO:Al overcoating the Ag, an a-Si:H intrinsic layer of varying thickness, and a conformal 80 nm thick layer of indium tin oxide (ITO). The ZnO:Al layer was used in all substrate-type a-Si:H solar cells to prevent the diffusion of Ag into the a-Si:H. The optical properties of ZnO:Al, a-Si:H and ITO were determined by spectroscopic ellipsometry measurements.

The modeling presented above exhibited the advantage of realistic conformal deposition conditions to design the devices with broadband absorption enhancement based on several different resonances. Localized resonances within the semiconductor played a key role in enhancing absorption on the blue side of the spectrum. The metal patterns on the back-contact were then used to couple red light in the waveguide modes of the cell. With the implementation of techniques such as nanoimprint lithography, these patterns can be fabricated over large areas inexpensively. Moreover, electromagnetic simulations have emerged as a critical and viable tool for optimizing the design of the structures. Through the simulation of different permutations, the roles of each of the interfaces in light trapping were identified. The authors also showed that Al is a viable back-contact material in these designs, with the potential for higher photocurrents than Ag.

On the basis of the modeling presented above, Polman et al [14] systematically designed and fabricated periodic and random arrays of nanoscatterers integrated in the back-contact of an a-Si:H solar cell, and demonstrated an extremely thin cell with broadband photocurrent enhancement in both the blue and red portions of the spectrum. The authors utilized substrate conformal imprint lithography (SCIL), a wafer-scale nanoimprint lithography process, to inexpensively replicate high-fidelity, large-area nanopatterns in silica sol-gel resist. An initial large-area master substrate was patterned using electron-beam lithography on a Si wafer. A bilayer stamp was molded from the master—consisting of a high-modulus polydimethylsiloxane (PDMS) layer holding the nanopatterns and a low-modulus PDMS layer—to bond the rubber to a thick glass support for in-plane stiffness. The designed nanopattern-imprinted silica sol-gel surfaces were overcoated with Ag via sputtering to form the metallic back-contact.

The designed individual nanostructures consisted of rounded plasmonic hemi-ellipsoidal nanostructures after coating with Ag. The rounded metal nanostructures were advantageous as they avoided the high parasitic absorption associated with sharp metallic features and allowed for the conformal growth of a-Si:H to produce both front and back textures. The top indium tin oxide (ITO) surface of the cell showed a pattern of nanodomes as a result of conformal depositions over the Ag back-contact. Solar cells were deposited over identical substrates. They consisted of Ag coating the patterned silica sol-gel, ZnO:Al deposited by sputtering, n-i-p a-Si:H of varying i-layer thickness, ITO and
evaporated Au finger contacts. The efficiency and the current-voltage measurement were performed and the following best values of efficiency ($\text{Eff}$), short-circuit current ($\text{I}_{\text{sc}}$), open-circuit voltage ($\text{V}_{\text{oc}}$) and fill factor (FF) among 1000 solar cells were obtained: $\text{Eff} = 9.60\%$, $\text{I}_{\text{sc}} = 16.94 \text{mA cm}^{-2}$, $\text{V}_{\text{oc}} = 0.864 \text{V}$, and $\text{FF} = 0.66$.

It is worth noting that the experimental trends corresponded well with those predicted by the simulation—including the strong enhancement in the blue portion of the spectrum. Since the electromagnetic simulation technique only accounts for optical absorption, but not carrier collection, the observed increase on the blue side of the spectrum was likely due to light trapping. The design of the pseudorandom arrays of resonantly scattering nanoparticles allowed for both an understanding of the ideal random patterns for broadband, isotropic angular response, and the realization of high-efficiency devices in thin semiconductor regions. Key to the design was an integrated understanding of the spatial frequencies and curvature of nanoscale scatterers that form back-reflectors coupling to waveguide modes and weakly coupled surface Mie scatterers coupling to localized modes.

For the fabrication of a solar cell, or a tandem solar cell architecture which traps sunlight efficiently, design on the basis of theoretical simulation calculations always plays an important role. With attention to both the electromagnetic as well as the electronic properties of the semiconductor, Li et al [15] developed exact three-dimensional (3D) simulations of plasmonic solar cells (PSC), linking both optical absorption and carrier transport together.

The authors performed a modular two-step 3D simulation based on the finite element method. The first step was to perform an exact electromagnetic calculation based on 3D Maxwell equations in the frequency domain. A single unit cell was used in conjunction with periodic Floquet–Bloch boundaries to represent the whole structure, and a standard AM1.5G spectrum was used as the incident light source. Linearly polarized light was used since the device is rotationally symmetric and insensitive to light polarization. The photo-generation rate extracted from the optical calculation was also used for the exact carrier transport calculations in the second step. This is based on two sub-modules simulating electron and hole transport, respectively, and one sub-module for electrostatic potential. The 3D transport equations were solved under solar injection and forward electric bias for the calculation of photocurrent and direct current. Finally, information on the solar cell performance, including external quantum efficiency (EQE), short-circuit current ($\text{I}_{\text{sc}}$), current-voltage (IV) curve, open-circuit voltage ($\text{V}_{\text{oc}}$), maximum output power density ($P_{\text{max}}$), and fill factor (FF) etc, can be obtained for the optimization of PSC design.

With the understanding of the strong effects of localized surface plasmon polaritons (LSPPs) on the electromagnetic processes at the metal surface, Paetzold et al [16] proposed a plasmonic light trapping concept based on LSPP-induced light scattering on the nanostructured Ag back-contacts of tandem thin-film silicon solar cells. Electromagnetic interaction between incident light and LSPP resonances in nanostructured Ag back-contacts was simulated with a three-dimensional numerical solver of the Maxwell equations. The design of the nanostructures was analyzed regarding their ability to scatter incident light into large angles and at low optical losses in the silicon absorber layers of tandem thin-film silicon solar cells.

The designed solar cell consisted of several layers (consecutively from back to front):

- Ag plasmonic nanostructured reflective back-contact,
- ZnO:Al transparent electrode,
- Hydrogenated microcrystalline silicon ($\mu$-Si:H),
- Hydrogenated amorphous silicon (a-Si:H),
- Glass substrate.

This design implies two advantages: first, instead of nanoparticles, the authors utilized a Ag back-contact as their preparation and implementation into the rear side of solar cells is relatively easy. Second, the Ag nanostructures are not in contact with the absorber layers and therefore no additional recombination losses take place.

The interaction of electromagnetic waves with a nanostructured back-contact was studied with a three-dimensional numerical solver of the Maxwell equations. The applied software was based on the finite element method (FEM) and discretized the Maxwell equations on a three-dimensional tetrahedral grid.

Red and near-infrared (NIR) photons (with $\lambda > 650 \text{ nm}$) are very poorly absorbed in the thin nanocrystalline silicon (nc-Si) absorber layers. To enhance the absorption of solar photons up to wavelengths of the band edge ($\lambda = 1100 \text{ nm}$) in nc-Si, a randomly roughened back-reflector of silver and zinc oxide (Ag/ZnO), which scatters incoming light in random directions, is often used. This scattering phenomenon makes it possible to increase the path length of the photons by $4\pi^2$ for completely lossless conditions. However, due to significant losses, the observed enhancement was considerably less than this. In [17] Biwas and Xu proposed a novel periodic plasmonic crystal (PC) back-reflector with a conformal nc-Si solar cell architecture that approached the semi-classical limit $4\pi^2$ when averaged over the entire spectrum of absorbed wavelengths. The simulations were based on the well-established scattering matrix approach, where the Maxwell equations are rigorously solved in Fourier space for both polarizations of the incident wave, with the electric and magnetic fields expanded in the Bloch waves. The structure was divided into layers in the z-direction. The dielectric function was periodic in two-dimensions within each layer. Scattering matrices for individual layers were found and convoluted to obtain the scattering matrix of the entire structure, from which the authors obtained the reflection and absorption rates at each incoming wavelength.

Enhanced absorption at long wavelengths occurred through a combination of two mechanisms: (i) plasmonic enhancement of light intensity at the periodic metallic back-reflector and (ii) diffraction resonances. Diffraction resonances gave rise to maxima in simulated absorption and
occurred when the phase difference of waves from the top and bottom of the absorber layer was a multiple of $2\pi$.

In brief, the authors have developed a conformal plasmonic crystal-based architecture for an nc-Si solar cell that has approached the classical limit of $4n^2$ for absorption averaged over the entire wavelength range of interest. Enhancements were due to both the plasmonic concentration of light at the back-reflector and diffraction resonances.

Further developing the preceding work [17] of Biwas and Xu, in [18] Biwas, Dalal et al demonstrated a photonic-plasmonic nanostructure for significantly enhancing the absorption of long-wavelength photons in a thin-film silicon solar cell with the promise of exceeding the classical $4n^2$ limit for enhancement. This enhancement can approach $\sim$50 in silicon. The authors systematically compared the device with a randomly-textured back-reflector to that with a carefully-designed periodic photonic-plasmonic back-reflector, and showed that the photonic-plasmonic structure is more effective in enhancing light absorption in thin-film Si solar cells.

The authors chose nanocrystalline silicon (nc-Si) as the absorber material—as it collects red and near-infrared photons up to the band edge (1100 nm)—and amorphous hydrogenated silicon (a-Si:H) to collect short-wavelength photons.

Before fabricating the device, the authors characterized randomly roughened back-reflectors by measuring total and diffuse reflectance. They selected annealed Ag and etched ZnO reflectors as benchmark ‘best’ reflectors because they had very high diffuse reflectance, exceeding 70% over the entire spectra range (400–1000 nm).

Nanocrystalline silicon (nc-Si) solar cells were deposited using plasma-enhanced chemical vapor deposition, employing H-profiling. An a-Si:H n$^-$ layer was grown on the substrates, followed by a very thin intrinsic a-Si:H seed layer and a thick nc-Si layer.

Optical and electrical characterizations were performed on the nc-Si:H solar cells. The authors measured I–V curves and external quantum efficiency (EQE) to obtain the wavelength-dependent photocurrent between 400 and 1100 nm for all devices to confirm the I–V curves. The EQE had a maximum of $\sim$90% near 530 nm. The authors used a $-1.0$ V bias measurement in the EQE to ensure the complete collection of photo-generated carriers. There was only a $\sim$2%–3% difference between the EQE at 0 V and $-1$ V.

The measurements were performed on the devices with different substrates. The lowest current was obtained for cells with a stainless steel (SS) substrate. Ag on SS improved the current by 13%. Etched ZnO + Ag gave a higher current. Annealed Ag or nanohole-imprinted substrates showed a 27% improvement over flat silver; finally the photonic-plasmonic structure gave the best result, showing an increase of 34% over flat silver.

Thus, the authors fabricated a controlled series of nc-Si solar cells on both photonic-plasmonic back-reflectors and randomly textured back-reflectors. The randomly textured ones were chosen to have a very high diffuse reflectance. The periodic back-reflector of the photonic-plasmonic nanostructures outperforms the best annealed Ag randomly textured one, illustrating the viability of photonic-plasmonic nanostructures for advanced photon harvesting.

### 3. Plasmonic enhancement in dye-sensitized solar cells

For fabricating silicon solar cells with high performance it is necessary to have advanced light-trapping concepts to enhance light absorption in thin silicon optically absorbing layers. There are two promising concepts: surface gratings allowing the control of scattering angles via discrete diffraction orders and Ag nanostructures of radii above 100 nm which scatter incident light with high efficiency and low absorption via localized surface plasmon resonance (LSPR). In [19] of Paetzold et al., these two concepts were combined in the plasmonic reflection grating back-contact. Half-ellipsoidal Ag nanostructures were arranged in a square lattice at the ZnO:Al/Ag back-contact of microcrystalline hydrogenated silicon (µc-Si:H) solar cells such that they formed a two-dimensional reflection grating.

In order to demonstrate the plasmonic light trapping concept of a plasmonic reflection grating back-contact, n-i-p substrate-type µc-Si:H solar cells were fabricated. First, nanostructured substrates with square-lattice-arranged nanocubes were prepared by an imprint process. On top of these substrates, a thick Ag layer and then a thick ZnO:Al layer were deposited by radio-frequency sputtering. Due to the nearly conformal deposition of Ag, the surface revealed half-ellipsoidal nanostructures with radii of around 100 nm and a height of around 80 nm, forming the plasmonic reflection grating back-contact surface. Afterwards, a µc-Si:H layer stack was deposited by plasma-enhanced chemical vapor deposition. For the front-contact, the authors used a thick ZnO:Al layer in combination with Ag finger electrodes.

An appropriate measure of the light trapping effect in solar cells is external quantum efficiency (EQE) in the semi-transparent region of the intrinsic µc-Si:H layer (wavelengths between 500 nm and 1000 nm). By convolving the EQE with the AM1.5 spectrum, the short-circuit current $I_{sc}$ was calculated. It was shown that the plasmonic light trapping concept enhanced the $I_{sc}$ from 17.7 mA cm$^{-2}$ to 21.0 mA cm$^{-2}$. Applying optical simulation, the working principle of the plasmonic light trapping concept was explained.

The plasmonic enhancement effect for increasing the conversion efficiency of photovoltaic devices may be limited when the bare metal nanoparticles are directly applied both inside and outside the active layer. This is because those nanoparticles could be the recombination centers for light-induced electrons and holes. Moreover, with plasmonic-related scattering and the local field enhancement effect, it is difficult to cover the whole wavelength range of the silicon response spectrum by only varying the size and shape of the nanoparticles. To overcome these drawbacks, in [20] Liu, Huang et al proposed applying a plasmonic metal-dielectric core-shell structure for increasing the conversion efficiency of the cells.
Colloidal gold nanoparticles (AuNPs) with a core-shell structure were synthesized by the standard sodium citrate reduction method. HAuCl₄·4H₂O and sodium citrate (referred to as citrate) were used as the starting material and reducing agent, respectively. With this simple method, the authors fabricated a stable, purple solution of citrate coated AuNPs, in which the citrate acted as an electrostatic stabilizing agent. As a result, surface recombination induced by the direct contact between metal and active material was effectively avoided. The size of the gold core and the thickness of the citrate shell can be controlled by adjusting the ratio of HAuCl₄ and citrate, reactant concentration, reaction temperature and reaction time.

The photocurrent response spectra of the silicon photovoltaic devices (with and without Au-citrate core-shell nanoparticles) were measured by a standard solar cell relative spectral response measurement system which included a tungsten-halogen lamp (OSRAM), a grating monochromator providing monochromatic light, a filter wheel for the elimination of multispectral images, a reference Si photodiode, a Si photodetector and a lock-in amplifier. With this system the photocurrent response of the device can be obtained under different wavelengths (from 300 to 1800 nm) and with high measurement repeatability (error < 1%).

Enhanced optical absorption by applying plasmonic core-shell AuNPs on top of wafer-based silicon photovoltaic devices has been investigated experimentally and theoretically. Obvious photocurrent enhancement was observed when the wavelength of incident light was above 800 nm. The highest enhancement, as high as 14%, was obtained around the wavelength of 1100 nm. Moreover, the simulation results helped the authors to understand increasing photocurrent performance in the near-infrared wavelength. It is worth noting that the enhancement effect was more obvious in the longer wavelength region, and large nanoparticle sizes corresponded to higher enhancement values.

In [21] Ouyang et al investigated the effect of localized surface plasmon resonance (LSPR) on light trapping in polycrystalline silicon thin-film solar cells and achieved a short-circuit current enhancement of 29% due to rear-located silver nanoparticles (AgNPs), increasing to 38% when combined with an additional back-reflector. It was known that the necessary conditions for effective plasmonic light trapping were high coupling efficiency, and large-angle scattering, and that to satisfy these requirements, the material, location, size and geometry of the nanoparticles as well as the local dielectric environment needed to be optimized. An optimization road-map for the plasmonic-enhanced light trapping scheme of self-assembled AgNPs was presented in a subsequent work of Ouyang et al [22]. This included a comparison of front- and rear-located nanoparticles, an optimization of the precursor Ag film thickness, an investigation of the different conditions of the nanoparticle dielectric environment and a combination of nanoparticles with other supplementary back-surface reflectors (BSRs).

The precursor amorphous silicon (a-Si) films were deposited by electron beam evaporation (EBE) on planar borosilicate glass substrates coated with silicon nitride (SiNₓ), which served as a diffusion barrier and an anti-reflection layer. After deposition, the films underwent solid phase crystallization, rapid thermal annealing and hydrogen plasma passivation. They were then processed into metalized cells. The cells were bifacial, and this bifacial feature enabled the comparison of light trapping performance between the front- and rear-located nanoparticles.

Ag nanoparticles were formed by the thermal evaporation of a thin layer of Ag film onto the cell surface followed by 50 min annealing at 200 °C in N₂ atmosphere. The particle size, shape and coverage were controlled by the thickness of the evaporated Ag film which was chosen to be 8, 12, 16, 20 and 24 nm. White acrylic paint was placed behind the nanoparticles to act as a pigmented diffuse BSR and further increase the photocurrent. The authors explored three ways of applying the white paint: directly onto the rear surface of the cell; on a flexible substrate which was then brought into close proximity to the cell’s back surface with a visible air gap; and onto an MgF₂ layer overcoating the nanoparticles. The size, shape and coverage of the nanoparticles were characterized from the images taken by scanning electron microscopy (SEM). Cell reflectance R and transmittance T were measured with a spectrophotometer and used to calculate the absorption coefficient A = 1 − R − T. The external quantum efficiency (EQE) was measured using a dedicated spectral response system and the short-circuit current density was calculated from the formula

\[ J_{sc} = q \int \lambda \text{EQE}(\lambda)S(\lambda), \]

where \( q \) is the electron charge and \( S(\lambda) \) is the standard spectral photon density of sunlight at the earth’s surface.

All the important factors for effective plasmonic-enhanced high trapping in polycrystalline Si thin-film solar cells were investigated. The optimum arrangement was to form AgNPs from a 16 nm thick precursor Ag film placed directly onto the rear Si surface of the cell, thereby directly increasing the short-circuit current by 27%. With the inclusion of a 350 nm MgF₂ space layer and white paint, the short-circuit current density enhancement further increased up to 44%. It was found that the AgNPs combined with a MgF₂ overcoating and white paint were the closest to an ideal BSR.

With the purpose of fabricating plasmonic nanostructures which are able to scatter incident light strongly in a large range so that it can be trapped inside the silicon layer keeping particle absorption to a minimum and, therefore, achieving broadband absorption enhancement, in [23] Gu, Jia et al proposed and demonstrated a novel nanoparticle geometry. This was based on large AgNPs combined with small particle nucleation, which effectively scattered light in a broad spectrum range with large oblique angles minimizing detrimental particle absorption. These nanoparticles were prepared by the simple, low-cost wet chemical synthesis method. The morphologies of the nanoparticles were well controlled by using different reactants and adjusting their concentrations.

The arbitrary coverage density of the nanoparticles on the solar cells was performed by tuning the concentration of AgNPs in the suspension. Enhancement was observed after
integrating the nucleated AgNPs with broadband optical response inside the dielectric layer at the rear side of the thin-film amorphous silicon solar cells with predesigned coverage density, consistent absorption, short-circuit photocurrent density \( (J_{sc}) \) and energy conversion efficiency \( (\eta) \). It was found that 200 nm nucleated silver nanoparticles at a 10% coverage density gave a superior performance, including the maximum \( J_{sc} \) and \( \eta \) enhancements of 14.26% and 23%, respectively. The highest efficiency achieved among the measured plasmonic solar cells was 8.1%.

In [24] Tan, Smets et al analyzed the main reasons leading to low plasmonic light trapping capability in hydrogenated microcrystalline silicon (\( \mu c\)-Si:H) solar cells and proposed to improve this capability by using plasmonic backreflectors (BRs) with broad angular scattering and low parasitic absorption. The authors investigated the correlation between the size of the AgNPs and both the angular scattering, as well as the parasitic absorption of the plasmonic BR. They demonstrated that by tuning the size of the AgNPs they could improve light trapping performance.

Each plasmonic BR had the following multilayer structure: glass/flat Ag/(ZnO:Al)/AgNPs/(ZnO:Al). The AgNPs were formed by a self-assembly method, and their size was tuned by the initial thickness of the as-deposited Ag film and the annealing temperature. Reflection measurements and angular resolved scattering were performed by standard spectroscopic methods. The n-i-p \( \mu c\)-Si:H solar cells with a \( \sim 2\ \mu m \) thick intrinsic absorber layer were fabricated by plasma-enhanced chemical vapor deposition. The solar cells were completed by sputtering an 80 nm thick indium tin oxide (ITO) layer and a Ag grid as the top electrode. The open-circuit voltage \( (V_{oc}) \) and fill factor \( (FF) \) were determined from current-voltage \( (I-V) \) measurements under an AM1.5G solar simulator. To better evaluate the light trapping, the external quantum efficiency (EQE) measurements were carried out at negative bias. The photocurrent was calculated from EQE curves by convolution with the photon flux of an AM1.5G solar spectrum between 300 and 1100 nm. The authors were finally able to show experimentally that using a plasmonic BR, the photocurrent of \( \mu c\)-Si:H solar cells could be enhanced by 4.5 mA cm\(^{-2}\).

For stabilizing and boosting the solar energy conversion efficiency of hydrogenated amorphous silicon (a-Si:H) solar cells, Shieh, Pan et al [25] proposed a sandwiched light trapping structure consisting of a capped aluminum-doped ZnO (AZO) thin-film, dispersed plasmonic AuNPs and a microstructured transparent conductive fluorine-doped tin oxide SnO\(_2\):F (FTO) electrode. Such a structure provided immunity to metal diffusion and a low-defect AZO/a-Si:H interface, where the AZO acted as a protective layer eliminating \( \text{H}^+ \) ion bombardment on the electrode substrate [26]. The low plasma power density for a-Si:H deposition also minimized ion bombardment on the substrate [27]. The AuNPs/AZO layer enhanced the absorption of green-red solar energy via the plasmonic effect, and the microstructured FTO functioned like a short-wavelength scatter, which increased ultraviolet-blue solar energy conversion. Because of this, the sandwich structure enhanced broadband light harvesting and reduced the defect density across the AZO/a-Si:H interface.

The proposal presented above on sandwiched plasmonic light trapping structures was implemented. The authors fabricated a-Si:H thin-film solar cells consisting of a hybrid plasmonic-structured AZO/AuNPs/FTO electrode and a-Si:H active layers of low-defect density with high photovoltaic efficiency and stability. The hybrid plasmonic light trapping structure exhibited a broadband light harvest, a high conversion efficiency of 10.1% and a slight photodegradation as small as 7% after light soaking. The good photovoltaic properties resulted from the introduction of a conformal AZO ultra-thin layer between the active layers and the AuNP-dispersed FTO substrate. The AZO layer encouraged the growth of the low-defect density a-Si:H layer, and thus improved interface properties between the a-Si:H active layer and the electrode. As a result, the plasmonic a-Si:H solar cells had an enhanced efficiency in the green-red band and a high resistance to photodegradation in the ultraviolet-blue wavelength range.

In [28] Brolo et al remarked that besides the strong enhancement of photocurrent in solar cells around the localized surface plasmon resonance (LSPR), the presence of AgNPs also led to a severe degradation of the photovoltaic (PV) performance in wavelength ranges located on the blue side of LSPR as well as to light absorption by particles due to the metallic interband transition. Moreover, destructive interference between the incident and scattered lights within a certain wavelength range shorter than the LSPR of particular NPs also induced a decrease in solar energy conversion efficiency. Therefore, the authors pursued the goal of experimentally tackling the problem of suppressed photocurrent for wavelengths shorter than the LSPR in plasmonic Si PV devices. The suppression effect was minimized by modifying the surface of the Si PV device with a mixture of Ag- and AuNPs, achieving an optimized overall photocurrent increase in the PV absorption spectrum in the visible range. The size of Ag- and AuNPs was well controlled by wet chemical synthesis. The surface coverage of the NPs was controlled by adjusting their concentration in the suspension deposited on a self-assembled monolayer of 3-aminopropyltrimethoxysilane (APTMS). Experimental investigation then provided strong support for surface plasmon-enhanced light trapping in PV devices.

Thus, the authors showed successfully that immobilizing mixed Ag- and AuNPs on the top of Si PV devices can improve their overall efficiency. The surface coverage and size dependence of Au NPs on external quantum efficiency (EQE) were studied systematically. \( \%\Delta \text{EQE}(\lambda) \) enhancement was strongly dependent on forward scattering efficiency and coincided with the LSPR. Au NPs larger than 80 nm led to increased \( \%\Delta \text{EQE}(\lambda) \) response above 600 nm. The highest \( \%\Delta \text{EQE}(\lambda) \) enhancement efficiency experimentally achieved with \( \sim670 \) nm AuNPs was \( \sim6\% \). More importantly, the authors have demonstrated experimentally tunable \( \%\Delta \text{EQE}(\lambda) \) enhancement by utilizing two types of (Ag and Au) metallic NPs. Use of the Ag: Au NP mixture maximized device efficiency over a broad spectral range (425 to over
1000 nm), and the overall power conversion efficiency, compared to the reference, increased by about 5%.

With attention to the role of the optical environment as a key factor to be considered when designing plasmonic solar cells, Park et al [29] investigated the optimum surface conditions for plasmon-enhanced light absorption in polycrystalline silicon (poly-Si) thin-film solar cells. This environment affects the surface plasmon resonance wavelength $\lambda_{\text{SPR}}$, scattering angle $\theta_{\text{scat}}$, scattering cross-section $Q_{\text{scat}}$ and coupling efficiency $f_{\text{coupl}}$. Since the environment for metallic nanoparticles (NPs) is normally a dielectric layer, layers such as silicon oxide, silicon nitride, titanium oxide, magnesium fluoride etc, can be used for separating the semiconductor and metallic NPs or for coating the metallic NPs to tune the spectral shift. To determine optimum surface conditions, the authors compared absorption between films or cells with metallic NPs formed on Si, and native SiO$_2$ layers, the $Q_{\text{scat}}$ of the NPs was calculated, and the potential short-circuit current densities $J_{\text{sc}}$ of each surface condition with NPs were compared. The authors also investigated how and why these surface conditions affect plasmon-enhanced light trapping.

In this work the authors employed AgNPs because their low parasitic light absorption and plasmonic resonance frequency is in the spectral range, which is important for poly-Si photovoltaic devices (400–1200 nm) if well tuned. A Ag precursor film with a thickness of 14 nm was deposited by thermal evaporation onto the Si cell rear surface, and it was then annealed at 230°C for 53 min in a nitrogen atmosphere to form NPs. The authors applied these parameters to the fabrication of Ag NPs because they showed the highest $J_{\text{sc}}$ enhancement in poly-Si thin-film solar cells based on previous research [30].

Cell reflectance and transmittance (T) were measured by standard spectroscopic methods and used to calculate absorption $A = 100\% − R − T$. Scanning electron microscopy (SEM) was used to confirm whether the Ag films were fully broken down into NPs. Ellipsometry was used to measure the thickness of the SiO$_2$ layer which formed on the surface of the cell. The electrical characteristics of the cell, such as $J_{\text{sc}}$, were used to compare the performance of the samples. To confirm the results from the calculated potential $J_{\text{sc}}$, the authors fabricated metallized poly-Si solar cells with three different surface conditions and measured the absolute $J_{\text{sc}}$ and $J_{\text{sc}}$ enhancement before and after NP formation. The sample with NPs on the native SiO$_2$ layer demonstrated the greatest $J_{\text{sc}}$ enhancement (33.31%). The sample with NPs on the Si film showed the second highest $J_{\text{sc}}$ enhancement. This result agreed well with the absorption measurements of the samples and supported the potential $J_{\text{sc}}$ estimation. The external quantum efficiencies (EQEs) of the three samples were also compared. All three samples without NPs showed a similar EQE at $\lambda > 500$ nm. After NP formation, the native SiO$_2$ and Si film samples showed better EQEs than the sample at $\lambda > 650$ nm because of increased absorption in this wavelength range. The native SiO$_2$ layer is therefore the optimum surface for plasmonic AgNPs in poly-Si thin-film solar cells.

With attention to the management of the light losses associated with AgNP-integrated plasmonic back-reflectors (BRs) in silicon wafer solar cells so as to ensure the high efficiency of plasmonic enhancement, in [31] Jia, Gu et al performed a comprehensive study of the light loss phenomenon in solar cells of this type. The influence of light loss on the light trapping of solar cells was investigated for three commonly used front-surface morphologies: planar cells, pyramid textured cells and honeycomb textured cells. The revealed insights are of particular importance for designing loss-managed plasmonic BRs for maximum light absorption enhancement in the Si layers of practical Si wafer solar cells, and in particular, textured solar cells. Each textured solar cell structure consisted of a ~75 nm SiN$_x$ anti-reflection coating, a ~180 μm silicon wafer with various front-surface morphologies, AgNPs embedded in the SiO$_2$ dielectric layer, and the Al BR. In the AgNP-integrated plasmonic reflector, AgNPs were embedded into the SiO$_2$ spacer layer providing effective surface passivation and metal isolation. The Al layer was then evaporated to provide rear reflection and enclosure. In order to find out the effects of Al reflection layer morphology on the associated plasmonic losses, another plasmonic BR was investigated. In this geometry a detached Al reflector with a flat surface was used.

The self-assembled AgNPs were fabricated by the widely used evaporation and annealing method. Due to surface tension, the film broke up and formed island NPs. The fabrication process of the solar cells was as follows: saw damage etching was first performed on p-type Si wafers. Alkali and acidic solution were used respectively to texture the surface of the Si wafers. The wafers were then put inside a POCl$_3$ diffusion furnace to form the n$^+$ emitter. The phosphosilicate glass formed during the diffusion process was then removed using a 5% HP solution. After this, the SiN$_x$ anti-reflection coating layer was deposited by the plasmonic-enhanced chemical vapor deposition (PECVD) system. An Al metal grid pattern was formed by photolithography on both the front and the rear surfaces of the solar cells. Then, a thin SiO$_2$ layer was deposited by an e-beam evaporator on the rear surface, followed by integration of the AgNPs and a SiO$_2$ overcoating. Finally a layer of Al was evaporated to produce the reflector.

So as to investigate solely the losses in the plasmonic back-reflectors, they were fabricated on glass slides without solar cell structures first and compared with the standard flat Al reflector on glass. The absorption of NPs can be derived simply from a direct measurement of reflection. The UV-Vis-NIR spectrometer with an integrating sphere setup was used to measure the total and diffused reflectance spectra in the range 300–1200 nm. It was observed that total reflectance was significantly reduced in the entire wavelength range for both plasmonic reflectors due to parasitic absorption in the metal, which is a detrimental factor when integrated with solar cells. Compared with the detached Al reflector, the evaporated Al reflector further reduced total reflection by approximately 10% in the wavelength range from 900 to 1200 nm, which indicated an even larger absorption loss.

The plasmonic back-reflectors were then integrated onto the solar cells with different front-surface morphologies.
External quantum efficiency (EQE) in the spectral range 800–1200 nm was measured for all solar cells and the short-circuit current density, \( J_{sc} \), generated by the photons in this range was calculated by integrating the EQE with the AM1.5G solar spectrum. The EQE enhancement was defined as the ratio of the EQE of the cells with the BR light trapping schemes to those without them. It was shown that the EQE of the planar solar cells with the standard Al reflector and two plasmonic reflectors exhibited obvious enhancement at wavelengths above 900 nm. The two plasmonic reflectors were found to be superior to the standard reflector which redistributed the reflected light due to scattering on the AgNPs, thereby increasing the light path inside the Si layers. Significant enhancement up to 2, 2.5 and 3-fold was found at a wavelength around 1150 nm for the standard reflector, the evaporated Al plasmonic reflector and the detached Al plasmonic reflector. The calculated \( J_{sc} \) enhancement in the wavelength range 800–1200 nm was 11%, 14% and 15%. However, the EQE and the \( J_{sc} \) enhancement of the three reflectors on the pyramid textured and honeycomb textured cells was less significant. This decrease was the result of decreased light absorption in the Si layers due to competitive absorption losses in the plasmonic reflectors. The percentage of light loss induced by the NPs was also calculated in [32]. It was shown that the percentage of particle-induced losses is smaller than the absorption enhancement for planar cells but larger than that for the two textured cells, leading to increased and decreased absorption in the Si layers respectively, and thereby an increased and decreased EQE.

4. Plasmonic enhancement in dye-sensitized solar cells

In the pioneering work [33] Grätzel and O’Regan successfully demonstrated the fabrication of a low-cost, high-efficiency solar cell comprising a transparent film of titanium dioxide (TiO₂) nanoparticles (NPs) and a monolayer of charge-transfer dye coated on the TiO₂ film to sensitize the film for light harvesting the dye-sensitized solar cell (DSSC). In the subsequent works of Grätzel et al [34–42], as well as of a large number of other authors, research on DSSCs developed rapidly and became a promising area of modern physics.

The proposal to exploit plasmonic effects for enhancing the efficiency of DSSCs was also presented a long time ago [43, 44]. In the present section of the review, we summarize the results of recent typical experimental works on the plasmonic enhancement of DSSCs.

For enhancing the performance of DSSCs, in [45] Ogale et al employed AuNP-loaded TiO₂NPs in the form of TiO₂–Au nanocomposite films to fabricate the working electrodes of the DSSCs. TiO₂ films containing solely TiO₂NPs were also prepared for comparison. The samples were characterized by various techniques: x-ray diffraction (XRD), diffused reflectance spectroscopy (DRS), Raman scattering, transmission electron microscopy (TEM), and electrochemical impedance spectroscopy (EIS). Current-voltage (I–V) characteristics were measured using a solar simulator. The measurements of incident photon to current conversion efficiency (IPCE) were performed using the quantum efficiency setup.

The cell performances of DSSCs based on only TiO₂, and of those based on TiO₂–Au nanocomposite electrodes were examined under 1 sun AM1.5 simulated sunlight. It was shown that in the case of nanocomposites, the short-circuit current density (\( J_{sc} \)) was about 13.2 mA cm\(^{-2} \), which was higher than the 12.6 mA cm\(^{-2} \) for TiO₂NPs. The higher \( J_{sc} \) value in the case of TiO₂–Au nanocomposites can be assigned to the plasmon-induced charge transfer from AuNPs to TiO₂ [46]. The open-circuit voltage (\( V_{oc} \)) of TiO₂–Au nanocomposites was 0.74 V while that of TiO₂NPs was 0.70 V. Furthermore, the fill factor (FF) of ∼61% for the case of TiO₂–Au films was higher than that for the case of TiO₂ films (∼56%). The increase of \( V_{oc} \) and FF was correlated to the decreased electron-hole recombination at the TiO₂–Au dye interface. By Au loading on TiO₂NPs, the IPCE improved from 5.0% to 6.0% (almost a 20% enhancement).

Instead of the conventional liquid electrolytes in the previously prepared DSSCs of [47] Cui, McGehee et al proposed and demonstrated the use of solid-state (ss) hole-transport material (HTM) to fabricate solid-state dye-sensitized solar cells (ss-DSSCs) and offered a viable pathway towards higher efficiency due to the fact that open-circuit voltage can be tuned by adjusting the highest occupied molecular orbital (HOMO) of the HTM. The use of solid-state materials also solved the potential leakage problems associated with the volatility and corrosiveness of liquid electrolytes.

An ss-DSSC was composed of a mesoporous TiO₂ photo-anode sensitized with a monolayer of dye, filled with HTM and capped by reflective metal contacts deposited on top of the active layer. It was shown that spectral enhancements in the photocurrent density can be obtained through: (i) the excitation of the localized surface plasmon resonances (LSPRs) of metallic NPs, (ii) scattering of light by metallic NPs into dielectric-like wave-guide modes of the solar cell and (iii) coupling to propagating surface plasmon polariton (SPP) modes. Whereas SPPs have their highest field intensity at the dielectric/ metal interface, they also exhibit a large penetration depth into the dielectric medium adjacent to the metal. The authors demonstrated that both SPP- and scattering-induced effects can be utilized to enhance the light absorption and efficiency of the solar cells through the use of plasmonic back-reflectors that consist of two-dimensional arrays of Ag nanodomes incorporated into ss-DSSCs by nanoimprint lithography (NIL).

Ss-DSSCs that incorporate plasmonic back-reflectors were tested under simulated AM1.5G illumination. Ss-DSSCs with planar, non-imprinted TiO₂ films and planar Ag electrodes were used as control devices. Two sensitizing dyes, Z907 and C220, were used. For the devices with Z907 dye the plasmonic nanostructure increased the short-circuit photocurrent (\( J_{sc} \)) by 16%, and the power conversion efficiency (PCE) increased from 3.15% to 3.8% for the control device. For the devices with C220 dye the \( J_{sc} \) increased by 12% and the PCE increased from 5.64% to 5.93%.
The plasmonic enhancement of DSSCs depends not only on the characteristics of the employed metal (Ag or Au) NPs and light absorbing dye molecules, but also on the geometrical configuration of the cells. With this interesting scientific idea, Cronin et al. [48] investigated and compared the plasmonic enhancement of DSSCs with different geometrical configurations, including those with AuNPs deposited on top of and embedded in the TiO2 electrode as well as those with light absorbing dye molecules deposited on top of and underneath the AuNPs. The mechanism of enhancement was attributed to the electromagnetic response of the plasmonic NPs coupling the light very effectively from the far-field to the near-field at the absorbing dye molecule monolayer, thereby increasing the local electron-hole pair (or exciton) generation rate significantly. The UV-Vis absorption spectra and photocurrent spectra provided further information regarding the energy transfer between the plasmonic NPs and the light-absorbing dye molecules. Based on scanning electron microscopy images, the authors performed electromagnetic simulations of these different geometric configurations, which corroborated the enhancement observed experimentally.

The authors fabricated and characterized the following three basic working electrode configurations:

1. A monolayer of Ru dye N719 deposited on top of Au NPs embedded in a TiO2 film.
2. A monolayer of Ru dye N719 on top of an evaporated 5 nm Au-island thin-film deposited on the TiO2 layer.
3. An evaporated 5 nm Au-island thin-film deposited on top of the dye monolayer and the TiO2 layer.

A conventional DSSC with a monolayer of Ru dye N719 on top of the TiO2 layer was also fabricated as a control. The absorption spectra of all the working electrodes were recorded by a spectrophotometer with an integrated sphere detector. The open-circuit photovoltage, short-circuit photocurrent and absorption spectra of all the working electrodes were recorded on top of the TiO2 layer was also fabricated as a control. The mechanism of enhancement was attributed to the electromagnetic response of the plasmonic NPs coupling the light very effectively from the far-field to the near-field at the absorbing dye molecule monolayer, thereby increasing the local electron-hole pair (or exciton) generation rate significantly. The UV-Vis absorption spectra and photocurrent spectra provided further information regarding the energy transfer between the plasmonic NPs and the light-absorbing dye molecules. Based on scanning electron microscopy images, the authors performed electromagnetic simulations of these different geometric configurations, which corroborated the enhancement observed experimentally.

Concerning the short-circuit photocurrent, the authors observed a large enhancement in the case of working electrode (i) compared to that of the conventional DSSC in the 460–730 nm wavelength range. The enhancement peak was 6.5% at a wavelength of 613 nm. In contrast, the overall photocurrent in the cases of the two electrodes (ii) and (iii) was also lower than that of the control for the same reasons presented above.

Concerning power conversion efficiency, the DSSC with the working electrode (i) also exhibited the highest performance of 2.28%, while that of the conventional DSSC was 0.94%. Those of the DSSCs with working electrodes (ii) and (iii) also showed a lower performance compared to that of the conventional one.

Metal (such as Ag or Au) nanoparticles (NPs) usually exhibit surface plasmon resonance, enhancing the electromagnetic fields in their vicinity and therefore enhancing optical absorption in materials located nearby (the plasmonic effect). When a metal NP is placed in contact with a semiconductor NP, the electron transfer between them (the charging effect) can also take place simultaneously. Having noted this phenomenon, Kamat et al. [49] proposed and experimentally demonstrated a method for isolating the two above-mentioned effects from each other by using core-shell-structured NPs with a Ag or Au core and a SiO2 or TiO2 shell instead of the corresponding bare-metal NPs. The authors have investigated the separate effects of each metal NP on the performance of DSSCs. Being an insulator, SiO2 acted as a barrier preventing the electron charging of the metal (Ag or Au) core, and thus only the plasmonic effect was exhibited. On the other hand, being a semiconductor, TiO2 was capable of transferring electrons to the metallic core and thus charged the Ag or Au core in the Ag@TiO2 or Au@TiO2 core-shell-structured NPs. In the experiment, with the use of TiO2- and TiO2-capped NPs the authors demonstrated that the efficiency of an N719 DSSC increased from 9.3% to 10.2% upon incorporation of 0.7% Au@SiO2 NPs, and to 9.8% upon the loading of 0.7% Au@TiO2 NPs. Since the AuNPs underwent charge equilibration with TiO2 and shifted the apparent Fermi level of the composite to a more negative potential, the Au@TiO2-NP-embedded DSSC exhibited a higher photo-voltage compared to that without for both Au@TiO2 and Au@SiO2.

In [50] Lee, Jung et al investigated the effect of plasmonic core-shell structures consisting of dielectric cores and metallic nanoshells on energy conversion in DSSCs. The structure of these core-shell particles was controlled to couple with visible light so that the visible component of the solar spectrum was amplified near the core-shell particles. In the core-shell particle TiO2 nanoparticle films, both the local field intensity and the light pathways were increased due to surface plasmons and light scattering. This in turn enlarged the optical cross-section of the dye sensitizers coated onto the mixed films, leading to the energy conversion efficiency enhancement of the DSSCs. The core-shell particles were distributed in the TiO2 films so that the entire photoelectrode was uniformly exposed to the plasmonic effect. The advantage of particulate nanostructures is that they excite localized surface plasmons regardless of the incidence geometry and polarization states of the incoming light.
The fabrication of dielectric@metal core-shell particles was performed by a two-step process. The first involved coating the Ag so that AgNPs formed on the surface of the SiO$_2$ particles. These AgNPs induced the growth of Ag films which then, in the second step, became continuous polycrystalline films playing the role of Ag shells. The above-mentioned evolution process of Ag nanoshells was clearly shown in the transmission electron microscopy (TEM) images. The x-ray diffraction (XRD) patterns of the bare SiO$_2$ particles and core-shell structures showed that the Ag nanoshells of the core-shell particles endured the thermal treatment essential for fabricating the DSSC photoanodes. The UV-Vis absorption spectra of the core-shell particles exhibited an absorption peak in the blue range when the core-shell particles were dispersed in de-ionized water. As the thickness of the Ag layer increased, the core-shell particles absorbed more light due to the evolution of the surface plasmons.

The core-shell particles were mixed with TiO$_2$NPs and chemically agglomerated to yield thick composite films. The UV-Vis absorption spectra of the thick composite films were measured in air using an integrating sphere. The authors demonstrated that the core-shell particles changed the photon passage in the composite film, and that the localized plasmon resonance in the core-shell-type composites increased the scattering and absorption of incoming light.

DSSCs were fabricated using N719 dye absorbed films. The overall conversion efficiency of the DSSC improved when the core-shell particles were added. Compared with pure TiO$_2$ films, the mixed films containing 22 vol% core-shell particles increased in efficiency from 2.7% to 4.0%. Given that a 22% decrease in the surface area of the composite film reduced the amount of absorbed dye, this increase in efficiency indicated that well-arranged core-shell particles can enhance the energy conversion capability of a dye molecule in the near field by up to 80%. The higher energy conversion efficiency of the core-shell particle-embedded DSSC was due to the increase in both the short-circuit current ($J_{sc}$) and the open-circuit voltage ($V_{oc}$). The $J_{sc}$ of DSSCs containing 22 vol% core-shell particles was 7.8 mA cm$^{-2}$, which was higher than the $J_{sc}$ of pure TiO$_2$-based DSSCs (5.9 mA cm$^{-2}$).

From the above-presented works on plasmonic DSSCs, we know that the incorporation of Au nanoparticles (NPs) into the bulk of DSSCs is detrimental for two reasons: firstly because of the corrosion of the Au NPs in the dye solution, and secondly due to the action of Au NPs as charge recombination centers. In [51] Snaiht et al. proposed to overcome these two drawbacks by coating each Au NP with a thin silica (SiO$_2$) shell and incorporating Au-SiO$_2$ core-shell nanostructures into DSSCs.

In principle, metal NPs could enhance absorption in the solar cell by either scattering light, enabling a longer optical path-length, by dipole–dipole interaction and resonant energy transfer, or by near-field coupling between the surface plasmon polaron and the dye excited state. To measure the fraction of scattering versus absorption from the mesoporous TiO$_2$ electrodes containing the Au-SiO$_2$ NPs, the authors performed UV-Vis transmission and reflection measurements in an integrating sphere obtaining the following result: at the peak absorption wavelength (525 nm), the total transmission $T$ is 36% and the total reflection is 8% indicating a total absorption of the film, $\alpha = 56\%$.

The photocurrent was significantly enhanced with the presence of Au-SiO$_2$ NPs, indicating that the light harvested from these ‘plasmonic’ components contributed directly to photocurrent generation.

For the solar cells fabricated with dye Z907, it was shown that the incorporation of Au-SiO$_2$NPs resulted in the increase of short-circuit photocurrent ($J_{sc}$) from 3.0 ± 0.8 to 5.0 ± 2.0 mA cm$^{-2}$, an increase of fill factor (FF) from 0.51 ± 0.13 to 0.59 ± 0.06, an increase of the overall power conversion efficiency from 1.2 ± 0.5% to 2.2 ± 1.0% and an increase of the optical density (OD) from 0.24 to 0.42. The increase in FF was unexpected and statistically relevant, indicating that the inclusion of Au-SiO$_2$NPs might have a broader influence than purely enhancing light absorption.

The plasmonic structures which were employed in the early works on the plasmonic enhancement of dye-sensitized solar cells (DSSCs) usually contained metal (Ag or Au) nanoparticles in direct contact with the dye and the electrolyte, resulting in the recombination and back reaction of the photogenerated carriers, as well as the corrosion of metal NPs by the electrolyte. These drawbacks can be prevented by employing Au@SiO$_2$NPs instead of bare AuNPs. However, by using the insulating SiO$_2$ shell, a part of the carrier photogenerated by the most absorption-enhanced dye molecules located on the surface of the shell would be lost due to difficulties with infection to SiO$_2$. To avoid this deficiency of Au@SiO$_2$ core-shell NPs, in [52] Hammond, Belcher et al. replaced them with Ag@TiO$_2$ core-shell nanostructures and incorporated these new NPs into the TiO$_2$ photoanode. This approach demonstrated the following advantages: first, the shell prevented any recombination and back reaction as well as protecting the Ag NPs from corrosion by the electrolyte. Second, the carriers could easily be transferred to the surrounding TiO$_2$NPs that were in contact with the shell. Third, by using a small Ag core and a very thin TiO$_2$ shell (2 nm) the effect of localized surface plasmons (LSPs) was maximized.

To investigate the effect of LSPs on device performance, the authors compared the performance of plasmon-enhanced DSSCs with standard DSSCs with only TiO$_2$NPs as photoanodes. The control DSSC showed a power conversion efficiency (PCE) of 3.1% whereas the plasmon-enhanced DSSC with Ag@TiO$_2$NPs exhibited a PCE of 4.4% (an increase of 42%), when the thickness of the photoanodes was 1.5 $\mu$m. For practical DSSCs, thicker photoanodes are required to absorb more light. The plasmon-enhanced DSSC achieved the highest PCE of 9.0% with a 15 $\mu$m thick photoanode, compared with the control DSSC reaching a highest PCE of 7.8% with a 20 $\mu$m photoanode. Therefore, by introducing Ag@TiO$_2$NPs into the TiO$_2$ photoanode, the PCE of the DSSC was improved by 15%, while the thickness of the photoanode was decreased by 25%.

Extending the results obtained in a previous work [52], Hammond, Belcher et al [53] proposed performing tunable localized surface plasmon (LSP)-enabled broadband light-
harvesting (LH) enhancement for high-efficiency panchromatic DSSCs. The authors demonstrated that multiple-core-shell oxide-metal-oxide plasmonic NPs were advantageous over nanostructures with other geometric configurations as they feature preservable plasmonic properties during device fabrication as well as adjustable localized surface plasmon resonance (LSPR) wavelengths $\lambda_{LSPR}$ of 600–1000 nm, at which near-field electromagnetic intensity is substantially enhanced.

Synthesis and optical characterization were performed for core-shell Ag@TiO$_2$ (AgT) and Au@TiO$_2$ (AuT) as well as multiple-core-shell TiO$_2$@Ag@TiO$_2$ (TauT) NPs. To study the LH of tunable LSP-enhanced DSSCs, different plasmonic NP-incorporated TiO$_2$ photoanodes were assembled onto the DSSCs. In 1.5 $\mu$m thick optically thin photoanodes, AgT, AuT and TauT NPs increased the incident photon-to-current conversion efficiency (IPCE) at $\lambda_{max}$ (maximum absorption wavelength $\sim$530 nm) by 45, 60 and 50%, respectively. Enhancement was maximized when $\lambda_{LSPR}$ was closest to $\lambda_{max}$. Similarly, at 700 nm TauT NPs increased IPCE the most by 80%, whereas AgT and AuT NPs enhanced IPCE by only 21 and 22% due to the large mismatch between the $\lambda_{LSPR}$ and the low-absorption wavelength region. Both experiments and simulations using the finite-difference time-domain (FDTD) method demonstrated that matching $\lambda_{LSPR}$ with the high-absorption or low-absorption wavelength region impacted the spectral response of LH differently. Matching $\lambda_{LSPR}$ with the high-absorption wavelength region enhanced LH in the already strongly absorbing region, which benefited the optically thin photoanodes. In contrast, matching $\lambda_{LSPR}$ with the low-absorption wavelength region improved the weakly absorbed part of the solar spectrum, which is of great importance for broadband LH in panchromatic solar cells.

In the above-presented experimental works on the plasmonic enhancement of DSSCs, spherical Ag and/or Au NPs were employed, and therefore device performance enhancement was restricted to fixed wavelength regions. Having noted that rod-like Ag and Au nanostructures have longitudinal plasmon absorption that can be tuned from visible NIR to IR regions by simply manipulating the aspect ratios of the rod, in [54] Chen et al. proposed and demonstrated the enhancement of low-energy sunlight harvesting in DSSCs by using plasmonic nanorods (NRs). However, for reducing the corrosion of the metal by electrolyte and avoiding charge recombination in conductors, instead of coating the metal with SiO$_2$ or TiO$_2$—as was done in the case of spherical metal NPs—the authors encapsulated the AuNR surface with a layer of Ag$_2$S. The final Ag$_2$S-coated Au NR was denoted AuNR@Ag$_2$S. The thickness of the Ag$_2$S layer was controlled at 2.0, 3.7 and 6.0 nm for investigation. The longitudinal absorption peak of AuNR@Ag$_2$S was at $\sim$685 nm (2 nm shell thickness), as the relatively strong irradiance of sunlight in this region ensures efficient surface plasmon resonance. At the same time, the absorption of N719 at around 685 nm is weak, and thus the incorporation of AuNRs@Ag$_2$S enhanced sunlight harvesting in this range. A AuNR@Ag$_2$S concentration of 1.69%, the device characteristics increased as follows: short-circuit current $J_{sc}$ from 8.79 to 11.10 mA cm$^{-2}$, open-circuit voltage $V_{oc}$ from 0.726 to 0.786 V, power conversion efficiency PCE: from 4.3 to 5.6%, and the incident photon-to-electron conversion efficiency (IPCE) showed significant broadening at 600–720 nm.

Thus, the use of the plasmonic effect was found to improve device performance by efficiently converting low-energy sunlight into electricity. A remarkable improvement of 37.6% in photocurrent generation at 600–720 nm was achieved. This approach to improving low-energy sunlight harvesting will have a wide range of applications due to the fact that the peak absorption of most conventional dye molecules centers at 500–600 nm. Since the optical response of Au NRs depends on their aspect ratios, harvesting sunlight at various longer wavelengths can be readily achieved by simply adjusting their aspect ratio.

5. Plasmonic titania solar cells

In the pioneering work [55], Tian and Tatsuma investigated photoelectrochemical processes in the visible light region induced by plasmon resonance in the gold nanoparticle-nanoporous titania composite (Au/TiO$_2$) prepared by the photocatalytic deposition of Au on TiO$_2$ film. The authors demonstrated the good agreement of the photoaction spectra for both open-circuit voltage ($V_{oc}$) and short-circuit current ($I_{sc}$) with the absorption spectrum of the gold nanoparticles (AuNPs) into the TiO$_2$ film. AuNPs were photoexcited due to plasmon resonance, and charge carrier separation was accomplished by the transfer of photoexcited electrons from AuNPs to the TiO$_2$ conduction band and the simultaneous transfer of compensative electrons from donors in the solution to the AuNP.

Measurements were performed with a photovoltaic (photocatalytic) cell with a Au/TiO$_2$ photoanode, a platinum wire cathode and a N$_2$-saturated acetonitrile ethylene glycol solution, and an electron donor. Among the donors examined, the redox couple FeCl$_2$/FeCl$_3$ was the best. The concentration ratio of Fe$^{2+}$ to Fe$^{3+}$ and the proportion between acetoniite and ethylene glycol in the solvent were optimized. The photocurrent action spectrum coincides very well with the absorption spectrum of AuNPs in TiO$_2$ film and showed a maximum incident photon-to-electron conversion efficiency (IPCE) (~12%) at around 560 nm. The addition of 0.2 M 4-nitrobenzoic acid to the electrolyte further improved the maximum IPCE up to 26%.

The wet photovoltaic cell fabricated with a Au/TiO$_2$ photoanode and a liquid electrolyte had several deficiencies, such as its instability, leaking and the vaporization of the electrolyte. To overcome these drawbacks, Tatsuma et al. [56] replaced the liquid electrolyte with different organic or inorganic solid hole transport materials (HTMs). Five HTMs were investigated: poly(N-vinylcarbazole) (PVK), N,N'-diphenyl-N,N'-bis-(3-methylphenyl)-1,1'-biphenyl)-4,4'-diamin (TPD), 4,4-bis [N-(1-naphthyl)-N-phenyl-amino] biphenyl (NPD), CuI and CuSCN. In the case of PVK, it was dissolved...
in a mixed toluene and cyclohexanone solvent. The films were kept in air to evaporate the solvent. The TPD and NPD layers were prepared in a similar manner using dichloromethane and toluene solution, respectively. The CuI and CuSCN layers were prepared on a preheated Au/TiO2 film by casting an aliquot of the acetonitrile solution of CuI and n-propylsulfide solution CuSCN (saturated), respectively. All the HTM layers were of about the same thickness. Finally, an Au back-contact was deposited on the semiconductor layer by sputtering. The film surfaces were observed using atomic force microscopy. The absorption spectra were collected with a UV-Vis spectrophotometer. An automatic polarization system was employed to measure the photoelectrochemical properties.

The short-circuit photocurrent, the open-circuit voltage and the photoaction spectra of all the prepared photovoltaic cells were experimentally determined. Then the maximum IPCE of each photovoltaic cell was calculated. The maximum IPCE of the cell with PVK had the lowest value of 0.0024%. The values of the short-circuit photocurrents had the following order: CuI > CuSCN > NPD > PVK, TPD, while the order of the values of the open-circuit voltage was CuI > CuSCN, NPD > PVK > TPD. These orders were consistent with the hole-mobility of the HTMs descending in the order CuI > CuSCN > NPD > PVK > TPD. Thus, hole-mobility in the bulk of the HTM controlled cell performance. The thickness of the HTM layer between TiO2 or AuNPs and the Au back-contact should be minimized—to improve cell performance.

To control the plasmon resonance of photovoltaic cells, Tatsuma et al [57] performed the layer-by-layer assembly of multilayer films composed of AuNPs and TiO2 nanostructures, and examined the effects of TiO2 nanosheets on the localized surface plasmon resonance (LSPR) properties of Au NPs. Negatively charged TiO2 nanosheets were synthesized by a well-established procedure. The glass substrate was immersed in a polyethylenimine (PEI) solution to introduce positive charges onto its surface. Then, the TiO2 nanosheets and poly(diallyldimethylammonium) chloride (PDDA) were sequentially adsorbed from the colloidal suspension of TiO2 nanosheets and PDDA solution, respectively, to obtain a new substrate of the form glass/PEI/TiO2/PDDA. By immersing this new substrate into the colloidal solution of the AuNPs, the authors obtained the layered nanostructure with one layer of TiO2 nanosheets:

$$M_1 = \text{glass/PEI/TiO2/PDDA/Au NPs.}$$

The films with this structure were covered again with a second layer of TiO2 nanosheets by employing another PDDA layer as electrostatic glue, and the deposition procedure was continued until the formation of the following layered nanostructure with two layers of TiO2 nanosheets:

$$M_2 = \text{glass/PEI/TiO2/PDDA/Au NPs/PDDA/TiO2/Au NPs.}$$

The deposition cycle was repeated, and the authors fabricated layered nanostructures with three or more layers of TiO2 nanosheets M3, M4.

Photoelectrochemical measurements were carried out in a conventional three-electrode, single-compartment glass cell. A N2-saturated acetonitrile solution containing tetra-n-butylammonium perchlorate (TBAP) and triethanolamine (TEOA) was employed as an electrolyte. Photocurrent, which was irradiated from the back of the working electrode, was measured at rest potential under visible light.

The authors demonstrated that the LSPR was significantly enhanced by the layered nanostructure M2 with two layers of TiO2 nanosheets. The interparticle plasmon coupling was at its maximum via a single intervening nanosheet layer, whereas three or more layers suppressed the coupling almost completely. The photocurrent increased as the LSPR was enhanced by covering it with TiO2 nanosheets. In addition, the polarity of photoresponses was controlled by changing the layering order of the AuNPs and titania nanosheets.

Recently Bach et al [58] proposed and experimentally demonstrated solid-state solar cells employing the composite material Au/TiO2 or Ag/TiO2 and exploiting the plasmonic enhancement of Au/TiO2 as well as Ag/TiO2. In these plasmonic titania solar cells, the photocurrent was generated by the photoexcitation of AuNPs or AgNPs adsorbed to TiO2, while the holes were transported through (2,2',7,7'-tetrakis(N, N'-di-p-methoxyphenylamine)-9,9'-spirobiﬂuorene) (Spiro-OMeTAD) as the HTM.

The absorption spectra of AuNP and AgNP layers after deposition onto the HTM were recorded together with the spectral photocurrent responses of the same layers. The observed strong increase in absorptivity and IPCE below 430 nm was due to the absorption and electron injection from the HTM Spiro-OMeTAD. The position of the plasmon resonance peaks of the metal NPs was red-shifted by about 60 nm (Au) and 80 nm (Ag) with respect to those in an aqueous environment due to the increase in refractive index of the environment and plasmon coupling between the NPs. The average peak IPCE values were 1.0% (AuNPs) and 0.5% (AgNPs). Maximum IPCE values of 1.8% (AuNPs) and 1.4% (AgNPs) were measured. Despite the fact that the NPs were only dispersed as a monolayer film, the prepared solar cells absorbed up to 37% of the incident photons at the plasmon resonance wavelengths. The average values of $V_{oc}$ were 120 mV (AuNPs) and 210 mV (AgNPs) under 1.5 solar irradiation using a 435 nm optical long pass filter to avoid direct TiO2 excitation. To demonstrate the sustainability of the charge separation process, these cells were illuminated close to their surface plasmon absorption peaks for 20 h using high intensity LEDs. The photocurrents generated by the nanoparticle-sensitized solar cells were found to be more stable than those generated by a dye-sensitized reference device.

It was found that photocurrent response closely followed the absorption spectrum of the NP layer. This indicated a close connection between surface plasmon excitation in the metal NPs and the charge separation process. However, the
physical driving mechanism of the process was still not known, and the authors discussed three different possible mechanisms.

The solid-state plasmon-enhanced TiO2-based photovoltaic cells investigated in [56, 58] were similar to the wet plasmon-enhanced TiO2-based photovoltaic (photocatalytic) cells presented in [55]—except for the fact that the liquid electrolyte was replaced by a solid-state HTM. Recently, Takahashi and Tatsuma [59] clearly demonstrated the use of photovoltaic cells without HTM with the structure In/TiO2/Au(Ag) NPs/ITO. This important result could be the first step in the development of sensitized solar cells without unstable factors—and at a lower cost of materials and fabrication than conventional cells.

The prepared In/TiO2/AuNPs/ITO cell was irradiated with monochromatic light and the photocurrent action spectrum obtained. It was roughly in accordance with the absorption spectrum of the TiO2-coated AuNPs, although the latter suffered from interference effects. The short-circuit current and open-circuit photovoltage in visible light were 105 μA cm⁻² and 0.41 V, respectively. These photoresponses were attributed to Au NPs, since the photoresponses were negligible for the cell In/TiO2/ITO without NPs. The maximum IPCE value of the solid-state In/TiO2/Au NPs/ITO cell (0.4%) was at least two orders of magnitude higher than the solid-state cell with PVK as an HTM. The sufficiently higher photoresponses of the TiO2-AuNP system without HTMs suggested that the photovoltage was generated at the TiO2-AuNP interfaces—likely due to electron injection from the resonant AuNP to TiO2 conduction band, resulting in a lowering of the AuNP Fermi level and a lifting of the electron level in the TiO2.

Thus, the authors developed simple solid-state In/TiO2/Au(Ag) NPs/ITO cells based on plasmon-induced charge separation. Their performance was much higher than that of the solid-state cell ITO/TiO2/Au(Ag) NPs/HTM/Au with HTMs. This result would encourage the development of solid-state sensitized photovoltaic cells with two-dimensionally distributed photosensitizers that are cost-effective and simply structured.

In the interesting work [60], Misawa et al. achieved the first success in plasmonic photoelectric conversion from visible to a near-infrared wavelength without deteriorating photoelectric conversion by using electrodes in which gold nanorods (AuNRs) were elaborately arrayed on the surface of TiO2 single-crystal electrodes via a top-down nanostructuring process. The prepared composite structure was clearly shown by scanning electron microscopy (SEM) images and its extinction spectra under irradiation of monochromatic light in different polarization states were recorded. A broad localized surface plasmon (LSP) band was observed around the wavelengths of 650 and 1000 nm. The measured spectra indicated that the transverse mode (T-mode) and longitudinal mode (L-mode) of identical and parallel NR arrays at 650 nm and 1000 nm, respectively, can be selectively excited by controlling the orientation of the linear polarization of the incident light.

The current-voltage (I–V) measurement under the irradiation of light in the wavelength range from 500 to 1300 nm was performed in two different cases: with a TiO2 electrode and with a Au/TiO2 electrode. At the applied voltage of 0.3 V, the authors observed an increase in photocurrent density from zero in the case of the TiO2 electrode to 30 μA cm⁻² when the Au/TiO2 electrode was used. It is interesting to note that this efficient photocurrent increase took place without using an electron donor.

According to the results of measurements on the action spectrum of the photocurrent generated by linearly polarized light, the IPCE values of the photocurrent were 6.3% and 8.4%, corresponding to the LSP bands in the T-mode at 650 nm and the L-mode at 1000 nm, respectively. The photocurrent induced by monochromatic light irradiation at wavelengths of 450, 650 and 1000 nm increased linearly with an increasing light intensity. No photocurrent was observed in the TiO2 single-crystal without Au NPs under the irradiation of light with a wavelength of 450 nm or longer. These facts clearly demonstrate that the electron injection from the Au NPs to the TiO2 single-crystal was induced by LSP excitation in the Au NRs.

In order to verify the relationship between photocurrent generation and plasmon excitation, the authors measured the IPCE spectra as functions of the peak wavelength of the plasmon resonance band and the density of the AuNPs. As a result, the shape and peak wavelength of the IPCE spectra were almost in accordance with those of the plasmon resonance band, and the IPCE value was highly dependent on the density of the AuNRs. Moreover, the TiO2 single-crystal deposited with AuNRs also generated a photocurrent under irradiation by infrared light in a wavelength range from 800 to 1300 nm as well as by visible light. Thus, the authors obtained excellent results compared with the previous work of other authors on similar subjects.

6. Conclusion and discussion

In the present review, we have summarized the advances in the research of light trapping and the plasmonic enhancement of thin-film silicon solar cells, dye-sensitized solar cells and solid-state titania-based photovoltaic devices (plasmonic titania solar cells). The results of the work presented above clearly demonstrate the solid-state titania-based photovoltaic cells without HTMs to be the most promising type of solar cell. Concerning the shape of plasmonic gold NPs, it was found that the nanorods exhibited priority compared to spherical NPs. The physical mechanism of electron injection from Au NRs to the conduction band of a TiO2 single-crystal would be through plasmon-induced hot electron generation at the interface between a metal nanoparticle and a metal-oxide single-crystal. A comprehensive review on the widespread implementation of this highly efficient mechanism was presented in a recent article by Clavero [61]. We believe that research on related scientific topics will achieve more and more success in the near future. This work is the continuation...
of our previous review on light trapping in organic solar cells [62].

Acknowledgments

The authors would like to express their deep gratitude to the Vietnam Academy of Science and Technology for the support.

References

[1] Atwater H A and Polman A 2010 Nature Mater. 9 205
[2] Catchpole K R and Polman A 2008 Opt. Express 16 21793
[3] Saeta P N, Ferry V E, Pacifici D, Munday J N and Atwater H A 2009 Opt. Express 17 20975
[4] Ferry V E, Munday J N and Atwater H A 2010 Adv. Mater. 22 4794
[5] Catchpole K R and Polman A 2008 App. Phys. Lett. 93 191113
[6] Beck F J, Polman A and Catchpole K R 2009 J. Appl. Phys. 105 114310
[7] Mokkapati S, Beck F J, Polman A and Catchpole K R 2009 Appl. Phys. Lett. 95 053115
[8] Nakayama K, Tanabe K and Atwater H 2008 Appl. Phys. Lett. 93 121904
[9] Spinelli P, Ferry V E, van de Groep J, van Lare M, Vershuuren M A, Schropp R E I, Atwater H A and Polman A 2011 Opt. Express 19 A303
[10] Ferry V E, Verschuuren M A, Li H B T, Schropp R E I, Atwater H A and Polman A 2009 Appl. Phys. Lett. 95 183503
[11] Ferry V E, Vershuuren M A, Li H B T, Vershuuren M A, Schropp R E I, Atwater H A and Polman A 2012 J. Opt. 14 024002
[12] Ferry V E, Polman A and Atwater H A 2011 ACS Nano 5 10055
[13] Ferry V E, Verschuuren M A, van Lare M C, Schropp R E I, Atwater H A and Polman A 2011 Nano Lett. 11 4239
[14] Li X, Hylton N P, Giannini V, Lee K-H, Ekins-Daukes N J and Meier S A 2011 Optics Express 19 A888
[15] Paetzold U W, Moulin E, Pieters B E, Carius R and Rau U 2011 Optics Express 19 A1219
[16] Biwas R and Xu C 2011 Optics Express 19 A664
[17] Bottger C, Chakravarty N, Pattanaik S, Slafer W D, Biwas R and Dalal VL 2011 Appl. Phys. Lett. 99 131114
[18] Paetzold U W, Moulin E, Michaelis D, Böttler W, Wächter C, Hagemann M, Meier M, Carius R and Rau U 2011 Appl. Phys. Lett. 99 181105
[19] Qu D, Liu F, Yu J, Xie W, Xu Q and Huang Y 2011 Qu D 2011 Appl. Phys. Lett. 98 131119
[20] Ouyang Z, Pillai S, Beck F, Kang O, Varlamov S, Catchpole K R, Campbell P and Green M A 2010 Appl. Phys. Lett. 96 261109
[21] Ouyang Z, Zhao X, Varlamov S, Tao Y, Wang J and Pillai S 2011 Prog. Photovolt: Res. Appl. 19 917
[22] Chen X, Jia B, Saha J K, Cai B, Stotes N, Qiao Q, Wang Y, Shi Z and Gu M 2012 Nano Lett. 12 2187
[23] Tan H, Sivec L, Yan B, Santbergen R, Zeman M and Smet A H M 2013 Appl. Phys. Lett. 102 153902
[24] Huang W H et al 2013 Appl. Phys. Lett. 103 073107
[25] Chantarat N, Hsu S H, Lin C C, Chiang M C and Chen S Y 2012 J. Mater. Chem. 22 8005
[26] Shen C H, Shieh J M, Huang J Y, Kuo H C, Hsu C W, Dai B T, Lee C T, Pan C L and Yang F L 2011 Appl. Phys. Lett. 99 033510
[27] Wang P H, Millard M and Brolo A G 2014 J. Phys. Chem. C 118 5889
[28] Park J, Park C and Varlamov S 2014 Appl. Phys. Lett. 104 033903
[29] Park J, Rao J, Kim T and Varlamov S 2013 Plasmonics 8 1209
[30] Zhang Y, Jia B, Ouyang Z and Gu M 2014 J. Appl. Phys. 116 124303
[31] Zhang Y, Stokes N, Jia B, Fan S and Gu M 2014 Sci. Rep. 4 4939
[32] O’Regan B and Gratzel M 1991 Nature 353 737
[33] Bai Y, Cao Y, Zhang J, Wang M, Li R, Wang P, Zakeeruddin S M and Grätzel M 2008 Nature Mater. 7 626
[34] Wang M et al 2008 Adv. Mater. 20 4460
[35] Ito S, Zakeeruddin S M, Compte P, Liska P, Kuang D and Grätzel M 2008 Nat. Photonics 2 639
[36] Qin H, Weng S, Xu M, Gao F, Jing X, Wang P, Zakeeruddin S M and Grätzel M 2008 J. Am. Chem. Soc. 130 9202
[37] Chen C-Y et al 2009 ACS Nano 10 3103
[38] Hardin B E, Hoke E T, Armstrong P B, Yum J H, Comte P, Torres T, Frechet J M J, Zakeeruddin S M, Krätzel M and McGehee M D 2009 Nat. Photonics 3 406
[39] Yella A, Lee H-W, Tsao HN, Yi C, Chandiran A K, Zakeeruddin M K, Dlau E W G, Yeh C-Y, Zakeeruddin S M and Grätzel M 2011 Science 334 629
[40] Yum J H, Baranoff E, Weng S, Zakeeruddin M K and Grätzel M 2011 Energy Environ. Sci. 4 842
[41] Kim H-S et al 2012 Sci. Rep. 2 591
[42] Zhao G, Kozuka H and Yoko T 1997 Sol. Energy Mater. Sol. Cells 46 219
[43] Wen C, Ishikawa K, Kishima M and Yamada K 2000 Sol. Energy Mater. Sol. Cells 61 339
[44] Muduli S, Gane O, Dhas V, Vijayamohanam K, Bogle K A, Valanoor N and Ogale S B 2012 Sol. Energy 86 1428
[45] Du L, Furube A, Yamamoto K, Haru K, Katoh R and Tachiya M 2009 J. Phys. Chem. C 113 6454
[46] Ding I-K et al 2011 Adv. Energy Mater. 1 52
[47] Hou W, Pavaskar P, Liu Z, Theiss J, Ayyol M and Cronin S B 2011 Energy Environ. Sci. 4 4650
[48] Choi H, Chen W T and Kamat P V 2012 ACS Nano 6 4418
[49] Ding B, Lee B J, Yang M, Jung H S and Lee K-J 2011 Adv. Energy Mater. 1 415
[50] Brown M D, Suteewong T, Kumar R S S, D’Innocenzo V, Petrozza A, Lee M M, Wiesner U and Snaith H J 2011 Nano Lett. 11 438
[51] Qi J, Dang X, Hammond P T and Belcher A M 2011 ACS Nano 5 7108
[52] Dang X, Qi J, Klug M T, Chen P-Y, Yun D S, Fang N X, Hammond P T and Belcher A M 2013 Nano Lett. 13 637
[53] Chang S, Li Q, Xiao X, Wong K Y and Chen H 2011 Energy Environ. Sci. 4 9444
[54] Tian Y and Tatsuura T 2005 J. Am. Chem. Soc. 127 7632
[55] Yu K, Sakai N and Tatsuura T 2008 Electrochemistry 76 161
[56] Sakai N, Sasaki T, Matsubara K and Tatsuura T 2010 J. Mater. Chem. 20 4371
[57] Reineck P, Lee G P, Brick D, Karg M, Mulvaney P and Bach U 2012 Adv. Mater. 24 4750
[58] Takahashi Y and Tatsuura T 2011 Appl. Phys. Lett. 99 181102
[59] Nishijima Y, Ueno K, Yokota Y, Murakoshi K and Misawa H 2010 J. Phys. Chem. Lett. 1 2031
[60] Clavero C 2014 Nat. Photonics 8 95
[61] Ha N B, Van Hieu N and Lam V D 2015 Adv. Nat. Sci.: Nanosci. Nanotechnol. 6 043002