Paper-Based Anti-Reflection Coatings for Photovoltaics

*Dongheon Ha, Zhiqiang Fang, Liangbing Hu, and Jeremy N. Munday**

For a typical air-semiconductor interface, >30% of the incident light is lost to reflection, and reducing this reflection is a key design principle for making high-quality solar cells. To reduce reflection, coatings are typically applied that rely on optical resonances (thin-film interference, plasmonics, Mie resonances, etc.); however, due to the nature of these effects, reflectivity is both wavelength and angle dependent, which is problematic for photovoltaic (PV) applications. Here we show the efficiency enhancement of a GaAs solar cell based on a new, paper-based anti-reflection coating (ARC) that produces a broadband, angle insensitive response, which results from the incoherent scattering associated with this textured cellulose material. Further, this ARC is inexpensive and made from an easily recyclable cellulose fiber.

Light management layers are important for all solar cells to ensure that light enters the device and that the absorption occurs in a region of the device that leads to carrier generation and collection. It is also advantageous to make solar cells thin, typically on the order of the minority carrier diffusion length to ensure carrier collection. Thus, reflective back layers are often used to increase the optical path length of light, which can be achieved through the use of highly reflective metal, dielectric, or Bragg stack layers.[1] Additionally, light management layers can be used to direct the light into regions where the absorption will lead to current generation rather than non-radiative recombination, which is likely to occur in passivating window layers or near metal structures. These optimized light management layers will thus depend on the type of device (e.g. absorption coefficient, carrier diffusion length, etc.), and are very important for thin films; however, a good ARC is necessary for all solar cells to ensure that light enters the device and enables absorption.

Traditional methods for anti-reflection coatings generally involve the deposition of single- or double-layer films in order to improve transmission by interference of the reflected light.[2] Because these techniques rely on interference, they are typically optimized for a wavelength in the middle of the solar spectrum and perform poorly at wavelengths far from the optimum or for grazing angles of incidence. Further, these anti-reflection coatings are manufactured by film deposition techniques such as chemical vapor deposition (CVD), sputtering, or evaporation, which have many disadvantages in terms of cost and the possibility of high temperature environments that are unsuitable for certain solar cell architectures. Thus, how cheaply and easily these layers can be made and how effective they are is of significant importance to future PV technologies.

One alternative to thin-film anti-reflection coatings is the use of metal or dielectric nanostructures.[3–22] The scattering properties of metal nanoparticles can be tuned by modifying their size, shape, or the surrounding environment and can lead to preferential forward scattering when placed on top of a high index substrate, such as a solar cell.[23] High index dielectric or semiconductor scattering objects can also yield improved forward scattering via coupling to Mie resonances.[4,24] These structures have shown improved anti-reflection characteristics; however, they are generally more complicated to fabricate, as they rely on subwavelength structures that require micro- and nano-scale lithography.

To circumvent the aforementioned difficulties, we present the use of an inexpensive and easy to process transparent paper for anti-reflection coatings. The transparent paper, consisting of cellulose fibers, is used to reduce the index contrast between air and the semiconducting absorber layer, which ultimately increases light absorption within the solar cell. Furthermore, surface texturing of the cellulose leads to angle insensitive behavior over all wavelengths under consideration. Because of the ease of this process, the approach described here is a potential candidate for next generation ARCs that replace the conventional coatings, which rely on high-cost, vacuum deposition methods. Additionally, these cellulose materials are lightweight, flexible, and recyclable. These properties have allowed for the recent use of cellulose papers as substrates for polymer solar cells and batteries.[25–30] These renewable and sustainable materials have good mechanical properties, low densities, low thermal expansion, tunable optical properties, and low toxicity.[25,31–39]

The transparent paper, which is fabricated by a papermaking technique using TEMPO-treated micro-sized wood fibers, has excellent optical properties (see Supporting Information). The paper used in this study not only has high optical transparency, but it also exhibits increased optical scattering. High transmittance allows most incident light to propagate though the paper and reach the active layer, while the optical scattering enables the possibility of increased path length. The scattering may be important for very thin solar cells; however, this feature is of less importance for optically thick devices, such as the one considered in this manuscript. In order to understand the stability of this paper under extended exposure to solar irradiation, the paper was exposed to AM 1.5G solar illumination in a solar simulator for 168 hours. No significant degradation of the optical properties was found (see SI); however, encapsulation in glass with UV protection may be beneficial for long-term applications.

D. Ha, Prof. J. N. Munday
Department of Electrical and Computer Engineering
Institute for Research in Electronics and Applied Physics
Building 223, Paint Branch Drive
University of Maryland
College Park, MD 20742–3511, USA
E-mail: jnmunday@umd.edu
Z. Fang, Prof. L. Hu
Department of Materials Science and Engineering
University of Maryland
College Park, MD 20742–2115, USA

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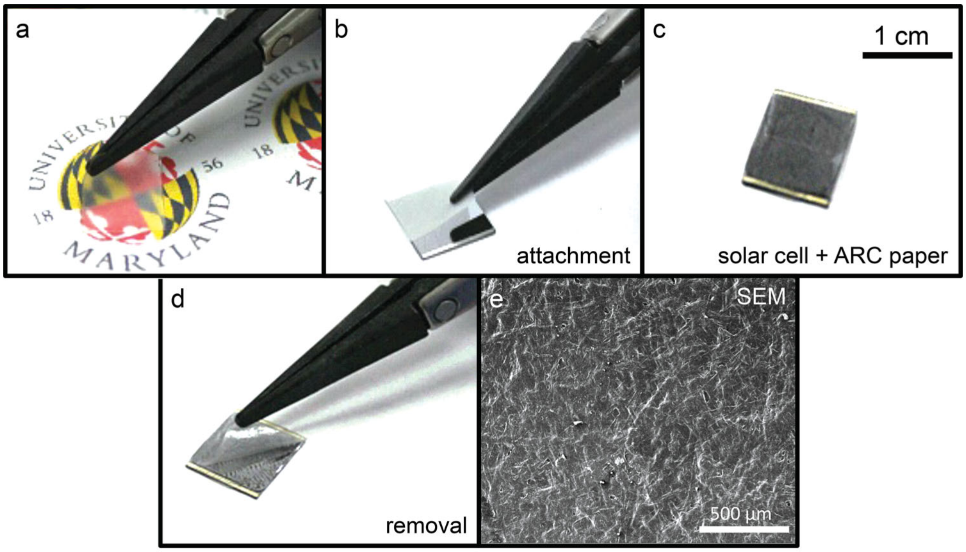

Figure 1. Transparent paper attachment and removal. a) The transparent cellulose paper. b) Attachment of the transparent paper onto a GaAs solar cell using PVA. c) The final cell with transparent paper on top. d) Detachment can be performed as need. e) SEM image of the transparent paper showing cellulose fibers.

In addition to the ease of fabrication, the paper can be easily attached (or removed) from the solar cell (**Figure 1**). During the attachment process, polyvinyl alcohol (PVA) is used to ensure adhesion, and the paper can be detached by mechanical peeling from the cell. The surface of the transparent paper was imaged by scanning electron microscopy (SEM). We find that randomly oriented, micro-sized wood fibers with an average length of 0.8 mm, width of 27 µm, and a total film thickness of 40–50 µm were produced during the process.

Addition of the transparent paper ARC to a GaAs solar cell (M-Comm) results in reduced reflection over all angles and wavelengths throughout the visible spectrum (**Figure 2**). The reflectivity is measured as a function of incident angle using an integrating sphere and monochromatic light. Figure 2 shows contour plots of the reflectivity as a function of incident angle (10° to 55°) and wavelength (400 to 900 nm). Without the transparent paper, the GaAs solar cell generally reflects approximately 35–45% of the incident light (Figure 2a); however, the addition of the transparent paper ARC reduces the reflection to approximately 15–25%. While a commercially available GaAs cell was used as a proof-of-principle demonstration, this coating technique can be applied to virtually any solar cell architecture ranging from Si, which dominates the PV market, to new thin film and/or flexible technologies.

The angular dependence of the reflectivity is also interesting to consider if one wishes to avoid the need for mechanical tracking elements to align the surface normal of the solar cell with the incident light from the sun. The angular dependence of the reflectivity is also reduced when the transparent paper ARC is used (Figure 2a,c). We believe that this reduced angular dependence is due to the surface texturing of the paper, which increases the likelihood of light entering the ARC, even at steep angles.

The reduction of the reflectivity can be explained using an incoherent reflection model and agrees well with the experimental data (Figure 2). The transparent paper consists of cellulose fibers (with refractive index n = 1.47),[40] which is very similar to that of PVA.[41] Because PVA is soaked into the transparent paper when processed, the refractive index of the mixture (transparent paper and PVA) is very similar to that of either the cellulose fibers or PVA alone. To better understand the enhancement in absorptivity, we consider an incoherent light propagation model based on the Fresnel equations with two different layers: the mixture of the transparent paper and PVA with a refractive index of ≈1.47 and the GaAs absorbing layer.[42] An incoherent model is used because of the texturing and the thickness of the layer rather than a coherent model, which would be appropriate for thin, flat films. At each incident angle, the reflectivity is calculated for each polarization and is given by

$$R_P = \left| \frac{n_1 \cos\theta_i - n_2 \cos\theta_t}{n_1 \cos\theta_i + n_2 \cos\theta_t} \right|^2 \tag{1}$$

and

$$R_S = \left| \frac{n_1 \cos\theta_t - n_2 \cos\theta_i}{n_1 \cos\theta_t + n_2 \cos\theta_i} \right|^2 \tag{2}$$

for P- and S-polarized incident illumination, respectively, where n_1 and n_2 are the refractive indices of the two media at the interface and θ_i and θ_t are the incident and transmitted angles from the surface normal. The slight polarization of our illumination source was determined and used to weight the calculated value of the reflectivity (see Supporting Information). Because there are multiple reflections as the rays travel through the film, a geometric series is calculated to determine the total reflection. Figure 2 shows that this incoherent model explains our data well. The calculation shows a slight increase in the reflectivity around 430 nm for samples both with and without the transparent paper ARC, which is not observed in the experiment. This feature is independent of the ARC and is likely due to a difference in the GaAs

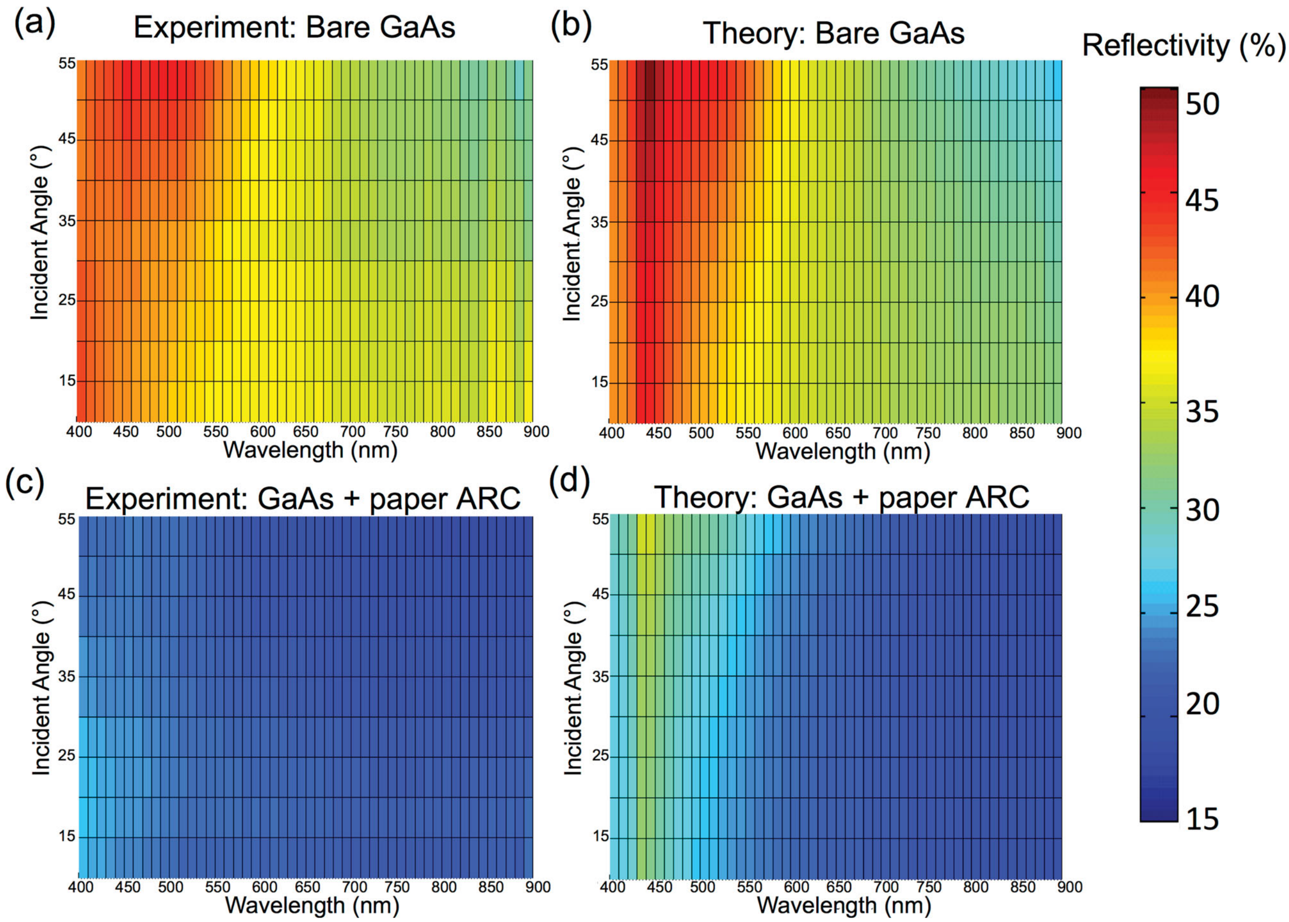

Figure 2. Transparent paper ARC reduces reflection over a wide range of incident angles and wavelengths. For the bare GaAs cell, contour plots of a) measured and b) calculated reflectivity as a function of incident angle (from 10° to 55°) and wavelength (from 400 nm to 900 nm) are in close agreement. The addition of a transparent paper ARC greatly reduces the measured reflection (c) over all angles and wavelengths. Calculations using an incoherent reflection model accurately predict the expected reduction of the reflectivity (d). Differences between the experiment and the calculations near $\lambda = 430$ nm are predominately due to differences in the optical properties of the GaAs used and are independent of the paper ARC.

index of refraction between that of Ref.[42] and of our actual sample.

Figure 3 shows a comparison between the measured and calculated reflectivity for incident illumination of $\lambda = 550$ nm for the GaAs cell both with and without the transparent paper ARC. The calculated reflectivity is in excellent agreement with the experimental data without the ARC; however, for large angles, the experimental data for the cell with ARC has reduced reflection when compared to the incoherent calculation assuming a flat interface. This can be attributed to the texturing of the cellulose fibers in the transparent paper, which allows for a more uniform reduction in the reflectivity.

The addition of the transparent paper ARC also improves the external quantum efficiency (EQE) of the solar cell measured at zero bias (**Figure 4**). EQE is the ratio of collected electron-hole pairs to the number of incident photons. Improved EQE is observed over the entire wavelength range from 400 to 900 nm. The enhancement in EQE throughout the entire wavelength range without any specific resonances is another indicator that the enhancement is not based on a simple anti-reflection effect but on the combination of the index contrast and surface

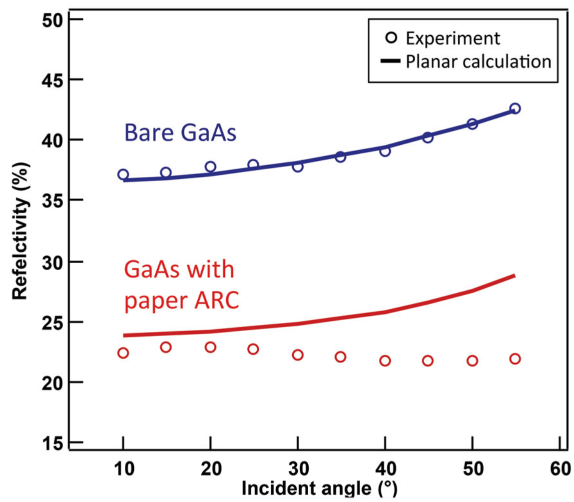

Figure 3. Measured (circles) and calculated (lines) reflectivity for both the bare GaAs cell (blue) and the GaAs cell with the transparent paper ARC (red) for $\lambda = 550$ nm. For the cell with the paper ARC, the reflectivity is both reduced and angle independent.

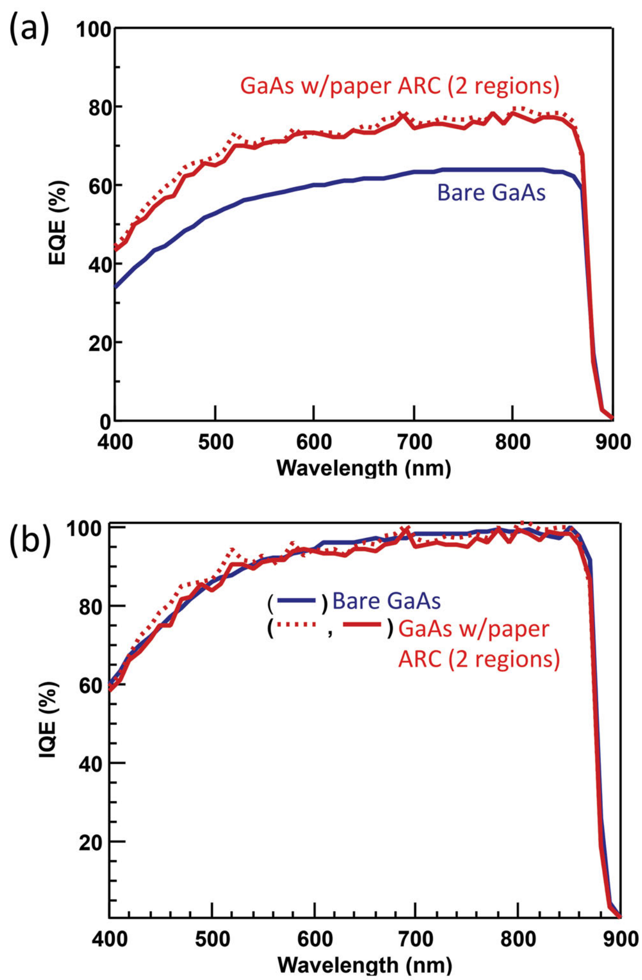

Figure 4. Quantum efficiency measurements for both structures. a) External quantum efficiency for the cell with the paper ARC (red) is improved over the entire wavelength range when compared to the bare GaAs cell (blue). b) Internal quantum efficiency is unchanged upon the addition of the ARC, showing no detrimental effect on carrier collection. Both EQE and IQE are measured on multiple regions (dotted and solid lines) of the cell and show no significant deviations.

texturing. The internal quantum efficiency (IQE) can be calculated by dividing the EQE by the absorptivity of the cell. As shown in Figure 4b, the IQE of the two different solar cells are almost identical over the entire wavelength range, showing that the process had no detrimental effects on the device's carrier collection.

The solar cell's efficiency is determined under AM 1.5G illumination using a solar simulator. **Figure 5** shows the measured current density-voltage (J–V) characteristics of the cell. The cell's electronic properties, which are extracted from the J–V curve, are given in **Table 1**. With the transparent paper ARC on top of the GaAs cell, the total power conversion efficiency is improved by 23.8%, from $\eta = 13.56\%$ to $\eta = 16.79\%$. The improvement is predominantly due to an increase in the short-circuit current density, J_{SC} (20.5%). A modest improvement in the fill factor, FF (2.6%) is also obtained; however, there is almost no change in the open-circuit voltage, V_{OC}. Because PVA has been used for

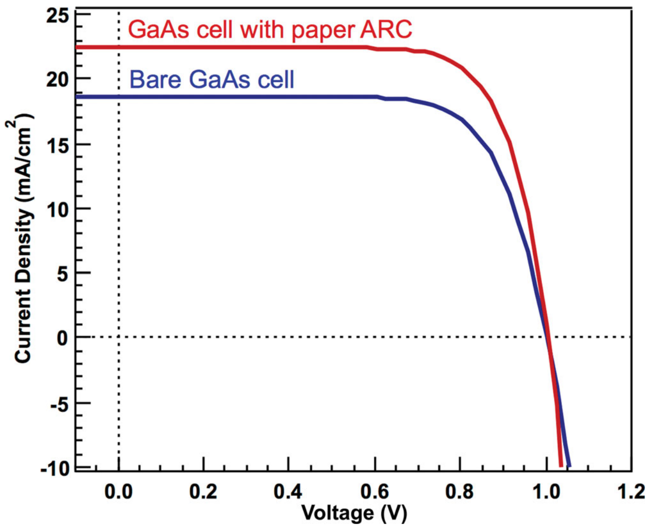

Figure 5. Current density vs. voltage characteristic for both the bare GaAs cell (blue) and the GaAs cell with the paper ARC (red). The addition of the paper ARC resulted in a 20.5% improvement in the short current density and a ≈23.9% improvement in the power conversion efficiency.

attachment of the transparent paper to the GaAs cell, the electrical characteristics of the cell with PVA alone is also measured to see if the PVA affects the properties of the solar cell. There is almost no change in V_{OC} and a slight increase in the efficiency (5.6%), mostly arising from the enhancement in the photocurrent due to the thin PVA layer acting as a poor quality ARC. We thus conclude that the PVA has minimal effect on the solar cell and can be used as a suitable attachment material.

In conclusion, we have developed a novel, transparent paper-based anti-reflection coating that improves solar cell efficiencies, for all angles of incident illumination, using a simple, earth abundant material and a room-temperature deposition process. The paper leads to a significant decrease in the light reflectivity and an improvement in the cell's power conversion efficiency. Due to a combination of index contrast and surface texturing, there is reduced reflection for all wavelengths, which is nearly independent of the incident angle. This approach leads to a large increase in J_{SC}, as well as a large increase in η. Because the transparent paper can be made with an easy, inexpensive and scalable process, this type of light scattering ARC is an excellent candidate for future solar technologies.

Table 1. Comparison of electrical properties between the bare GaAs cell and the GaAs cell with transparent paper ARC. Data represent the average of 7 measurements, and the uncertainties correspond to the standard deviation of the mean.

	V_{OC} [mV]	J_{SC} [mA cm^{-2}]	FF [%]	Efficiency [%]
Bare GaAs cell	1001.9 ± 0.3	18.67 ± 0.01	72.5 ± 0.5	13.55 ± 0.10
GaAs cell with paper ARC	1004.0 ± 0.5	22.49 ± 0.01	74.4 ± 0.2	16.79 ± 0.03
Enhancement from the bare GaAs cell [%]	0.21	20.46	2.62	23.91

Experimental Section

Fabrication of Transparent Paper: 0.45 g TEMPO-oxidized bleached sulfate softwood pulp was dispersed into deionized water with a concentration of 0.1% by weight using a magnetic stirrer. The solution was stirred for 5 minutes to get homogeneous suspension. The prepared pulp was then poured into a Buchner funnel with a filter membrane (Durpore Membrane, PVDF, 0.65 μm) to fabricate transparent paper by vacuum filtration. The film and filter membrane were placed between a stack of regular filter papers and dried under mechanical pressure.

Attachment of Transparent Paper to the GaAs Cell: The transparent paper was cut into a rectangle with an area of 1 cm × 1 cm for attachment to the cell. To improve cohesive strength between the transparent paper and the GaAs cell, 300 μL of polyvinyl alcohol (PVA) solution (5% by weight) was used as a binder, and the trimmed transparent paper was carefully placed on the PVA-covered cell to assure that the transparent paper covered the entire active area. The laminated sample was then dried at room temperature.

Supporting Information

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

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[1] P. Bermel, C. Luo, L. Zeng, L. C. Kimerling, J. D. Joannopoulos, *Opt. Express* **2007**, *15*, 16986.
[2] A. Luque, S. Hegedus, *Handbook of Photovoltaic Science and Engineering* John Wiley and Sons, United Kingdom **2011**.
[3] V. E. Ferry, J. N. Munday, H. A. Atwater, *Adv. Mater.* **2010**, *22*, 4794.
[4] P. Spinelli, M. A. Verschuuren, A. Polman, *Nat. Commun.* **2012**, *3*, 692.
[5] H. R. Stuart, D. G. Hall, *Appl. Phys. Lett.* **1998**, *73*, 3815.
[6] Ragip A. Pala, Justin White, Edward Barnard, John Liu, Mark L. Brongersma, *Adv. Mater.* **2009**, *21*, 1.
[7] H. A. Atwater, A. Polman, *Nat. Mater.* **2010**, *9*, 205.
[8] J. N. Munday, H. A. Atwater, *Nano Lett.* **2010**, *11*, 2195.
[9] J. Grandidier, D. M. Callahan, J. N. Munday, H. A. Atwater, *Adv. Mater.* **2011**, *23*, 1171.
[10] H. Park, D. Shin, G. Kang, S. Baek, K. Kim, W. J. Padilla, *Adv. Mater.* **2011**, *23*, 5796.
[11] I. K. Ding, J. Zhu, W. Cai, S.-J. Moon, N. Cai, P. Wang, S. M. Zakeeruddin, M. Grätzel, M. L. Brongersma, Y. Cui, M. D. McGehee, *Adv. Energy Mater.* **2011**, *1*, 51.
[12] Z. Tang, A. Elfwing, J. Bergqvist, W. Tress, O. Inganäs, *Adv. Energy Mater.* **2013**, *3*, 1606.
[13] B. Niesen, B. P. Rand, P. Van Dorpe, D. Cheyns, L. Tong, A. Dmitriev, P. Heremans, *Adv. Energy Mater.* **2013**, *3*, 145.
[14] J. You, X. Li, F.-x. Xie, W. E. I. Sha, J. H. W. Kwong, G. Li, W. C. H. Choy, Y. Yang, *Adv. Energy Mater.* **2012**, *2*, 1203.
[15] I.-K. Ding, J. Zhu, W. Cai,S.-J. Moon,N. Cai,P. Wang, S. M. Zakeeruddin, M. Grätzel, M. L. Brongersma, Y. Cui, M. D. McGehee, *Adv. Energy Mater.* **2011**, *1*, 52.
[16] X. Li, W. C. H. Choy, L. Huo, F. Xie, W. E. I. Sha, B. Ding, X. Guo, Y. Li, J. Hou, J. You, Y. Yang, *Adv. Mater.* **2012**, *24*, 3046.
[17] J. Weickert, R. B. Dunbar, H. C. Hesse, W. Wiedemann, L. Schmidt-Mende, *Adv. Mater.* **2011**, *23*, 1810.
[18] Q. Gan, F. J. Bartoli, Z. H. Kafafi, *Adv. Mater.* **2013**, *25*, 2385.
[19] J. Grandidier, D. M. Callahan, J. N. Munday, H. A. Atwater, *IEEE J. Photovoltaics* **2012**, *2*, 123.
[20] J. Grandidier, R. A. Weitekamp, M. G. Deceglie, D. M. Callahan, C. Battaglia, C. R. Bukowsky, C. Ballif, R. H. Grubbs, H. A. Atwater, *Phys. Stat. Solidi A* **2013**, *210*, 255.
[21] K. J. Yu, L. Gao, J. S. Park, Y. R. Lee, C. J. Corcoran, R. G. Nuzzo, D. Chanda, J. A. Rogers, *Adv. Energy Mater.* **2013**, *3*, 1401.
[22] D. M. O'Carroll, C. E. Hofmann, H. A. Atwater, *Adv. Mater.* **2010**, *22*, 1223.
[23] C. F. Bohren, D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons, New York **1983**.
[24] L. Cao, P. Fan, A. P. Vasudev, J. S. White, Z. Yu, W. Cai, J. A. Schuller, S. Fan, M. L. Brongersma, *Nano Lett.* **2010**, *10*, 439.
[25] Y. Zhou, et al., *Sci. Rep.* **2013**, *3*, 1536.
[26] F. Wang, Z. Chen, L. Xiao, B. Qu, Q. Gong, *Sol. Energy Mater. Sol. Cells* **2010**, *94*, 1270.
[27] T.-S. Kim, S.-I. Na, S.-S. Kim, B.-K. Yu, J.-S. Yeo, D.-Y. Kim, *Phys. Stat. Solidi Rapid Res.* **2012**, *6*, 13.
[28] A. Hübler, B. Trnovec, T. Zillger, M. Ali, N. Wetzold, M. Mingebach, A. Wagenpfahl, C. Deibel, V. Dyakonov, *Adv. Energy Mater.* **2011**, *1*, 1018.
[29] H. Zhu, Z. Xiao, D. Liu, Y. Li, N. J. Weadock, Z. Fang, J. Huang, L. Hu, *Energy Environ. Sci.* **2013**, *6*, 2105.
[30] H. Zhu, Z. Fang, C. Preston, Y. Li, L. Hu, *Energy Environ. Sci.* **2013**.
[31] J. Vartiainen, T. Pöhler, K. Sirol, L. Pylkkänen, H. Alenius, J. Hokkinen, U. Tapper, P. Lahtinen, A. Kapanen, K. Putkisto, P. Hiekkataipale, P. Eronen, J. Ruokolainen, A. Laukkanen, *Cellulose* **2011**, *18*, 775.
[32] N. Lin, J. Huang, A. Dufresne, *Nanoscale* **2012**, *4*, 3274.
[33] N. Lavoine, I. Desloges, A. Dufresne, J. Bras, *Carbohydrate Polymers* **2012**, *90*, 735.
[34] Y. Habibi, L. A. Lucia, O. J. Rojas, *Chem. Rev.* **2010**, *110*, 3479.
[35] R. J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood, *Chem. Soc. Rev.* **2011**, *40*, 3941.
[36] D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, A. Dorris, *Angew. Chem. Int. Edn.* **2011**, *50*, 5438.
[37] L. Hu, G. Zheng, J. Yao, N. Liu, B. Weil, M. Eskilsson, E. Karabulut, Z. Ruan, S. Fan, J. T. Bloking, M. D. McGehee, L. Wågberg, Y. Cui, *Energy Environ. Sci.* **2013**, *6*, 513.
[38] I. Siró, D. Plackett, *Cellulose* **2010**, *17*, 459.
[39] H. Zhu, S. Parvinian, C. Preston, O. Vaaland, Z. Ruan, L. Hu, *Nanoscale* **2013**, *5*, 3787.
[40] S. N. Kasarova, N. G. Sultanova, C. D. Ivanov, I. D. Nikolov, *Opti. Mater.* **2007**, *29*, 1481.
[41] S. Hayashi, K. Asada, S. Horiike, H. Furuhata, T. Hirai, *J. Colloid Interface Sci.* **1995**, *176*, 370.
[42] E. D. Palik, *Handbook of Optical Constants of Solids Academic*, New York **1998**.