

Toward Efficient Carbon Nitride Photoelectrochemical Cells: Understanding Charge Transfer Processes

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Photoelectrochemical cells (PECs) are a promising technology for the production of renewable energy by converting the sun light into electrical and chemical energy.^[1,2] The common PEC configuration is based on a photoanode, electrolyte solution (with or without redox couple), and a counter electrode. In a typical PEC, the photoanode is composed of a light harvester attached to a wide band gap semiconductor (i.e., TiO₂, ZnO) that serves as electrons acceptor layer while the holes are transferred to the counter electrode through the electrolyte solution.^[3] In order to achieve efficient PEC, a proper kinetic balance between the different charge transfer reactions taking place in the PEC must be accomplished.^[4,5] Particularly, in the photoanode, excited states electrons of the light harvester must be injected into the conduction band of a wide band gap semiconductor prior their self-recombination (either radiatively or nonradiatively). Besides, holes in the absorber must be transferred to the electrolyte before they recombine with the injected electrons in the semiconductor conduction band.^[6] In overall, long-live excitons, fast electron and hole separation and slow recombination dynamics are mandatory in order to obtain proper photoanodes in efficient PCE.^[7]

As a metal-free semiconductor, graphitic carbon nitride (g-C₃N₄) is attracting growing attention in the past few years due to its successful operation in various applications. In particular, it has been widely studied as a photocatalyst and electrocatalyst for water splitting and oxygen reduction reactions,^[8–13] degradation of pollutants,^[14] and in the field of heterogeneous catalysis.^[15] More recently, we and others showed that C₃N₄ can be used in photoelectronic devices, such as organic solar cells,^[16] light emitting diode,^[17] and photoelectrochemical cells.^[18–22] The PEC operation is considered to be more complicated compared to the photocatalysis process due

to the necessity to establish a direct contact between the active materials (C₃N₄) and the wide band gap semiconductor and the need of interparticle charge migration to the electrode.^[23–25] Lately, we have succeeded to sensitize TiO₂ with C₃N₄ by in situ deposition method that resulted in the formation of direct chemical bond between the TiO₂ and the C₃N₄. The intimate contact between TiO₂ and C₃N₄ led to the absorption extension to longer wavelengths due to creation of new energy transfer paths between the materials. Moreover, the TiO₂/C₃N₄ system exhibited promising photocurrent densities in the presence of polysulfide as the redox electrolyte.^[26] However, in comparison to the theoretical current densities the performances of this system are still low. In order to improve the cell performance, the understanding of the charge transfer reactions that limit the PEC efficiency, especially in the photoanode, is highly desired.

Herein, we studied the charge recombination process between C₃N₄ and mesoporous TiO₂ in a photoelectrode configuration using laser transient absorption spectroscopy (L-TAS). In addition, we determined the electron injection rate from the C₃N₄ excited states to the TiO₂ conduction band by steady state and time resolved photoluminescence. Finally, the hole extraction kinetics using various liquid electrolytes and solid state hole conductors were also studied in detail. Our measurements indicate that the photoexcited electrons from C₃N₄ can be efficiently injected to the TiO₂ conduction band, the recombination between electrons and holes from the TiO₂ conduction band and the C₃N₄ valence band, respectively, is found to be relatively slow, thus allowing long-live charge separation. However, the hole transfer to the electrolyte was found to be the limiting process during the PEC operation. This understanding of the processes taking place within C₃N₄/TiO₂ photoanode can lead to the efficient C₃N₄-based PEC cells and photovoltaics solar cell via rational selection of hole conductor and smart electrode design.

The C₃N₄ electrodes were prepared according to our previous report.^[26] Briefly, the C₃N₄ was deposited onto mesoporous TiO₂ (which was grown on FTO glass) and nonconductive glass, respectively, by using cyanuric acid-melamine (CM) supramolecular complex as the precursor. The CM precursor was placed on top of TiO₂ electrodes or glass, totally covering the substrates and afterward the system was heated to 550 °C under nitrogen atmosphere (see also Figures S1 and S2, Supporting Information). After that the electrodes were fully characterized by a range of techniques.^[26]

The important processes in PEC are shown in **Figure 1**. Under illumination electron–hole pairs are formed (path 1). For efficient PEC the electrons should be further injected into the electron acceptor layer (path 2) while the holes are expected to

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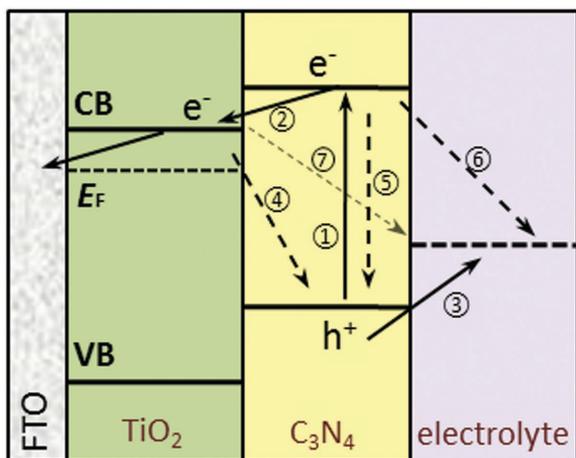


Figure 1. Schematic energy diagrams in the $\text{TiO}_2/\text{C}_3\text{N}_4/\text{electrolyte}$ system under light excitation and the proposed charge transfer mechanism (paths 1, 2, and 3, charge excitation and transfer; paths 4, 5, 6, and 7, charge recombination).

be extracted by the redox electrolyte (path 3). In contrary, the recombination of electrons and holes within the cell could negatively affect the total efficiency (paths 4–7). Consequently, the charge injection and recombination as well as the hole extraction have been studied in $\text{C}_3\text{N}_4/\text{TiO}_2$ electrodes. The electron

injection from the C_3N_4 excited states to the TiO_2 conduction band (Figure 1, Path 2) was studied through steady state and time resolved photoluminescence experiments (Figure 2a,b and Figure S3, Supporting Information). The emission spectrum of C_3N_4 supported on glass presents a wide band centered at 510 nm (Figure 2a). This emission is efficiently quenched when the C_3N_4 was deposited on the TiO_2 . In order to discard different processes from emission quenching such as TiO_2 photon absorption at 366 nm, UV-vis spectra of bare TiO_2 after and before C_3N_4 deposition have been compared in Figure S4 (Supporting Information). In the $\text{C}_3\text{N}_4/\text{TiO}_2$ spectrum the contribution of the bare TiO_2 has been subtracted, therefore, the $\text{C}_3\text{N}_4/\text{TiO}_2$ spectrum is showing solely the C_3N_4 contribution. The absorption of C_3N_4 at 366 nm is more than ten times higher than the one of TiO_2 . As consequence, emission intensity decrease of the $\text{C}_3\text{N}_4/\text{TiO}_2$ can be only attributed to the C_3N_4 excited states quenching. In addition, the emission spectra and the time correlated experiments were normalized with absorbance at excitation wavelength to dismiss the effect of the films absorbance due to differences in the C_3N_4 layers thickness (see Figure S3, Supporting Information).

The time correlated photoluminescence showed that the C_3N_4 emission lifetime is in the range of hundreds of nanoseconds. From the emission quenching of the C_3N_4 deposited onto TiO_2 , compared to C_3N_4 deposited on glass, we can assume that the yield of electron injection is higher than 90% upon

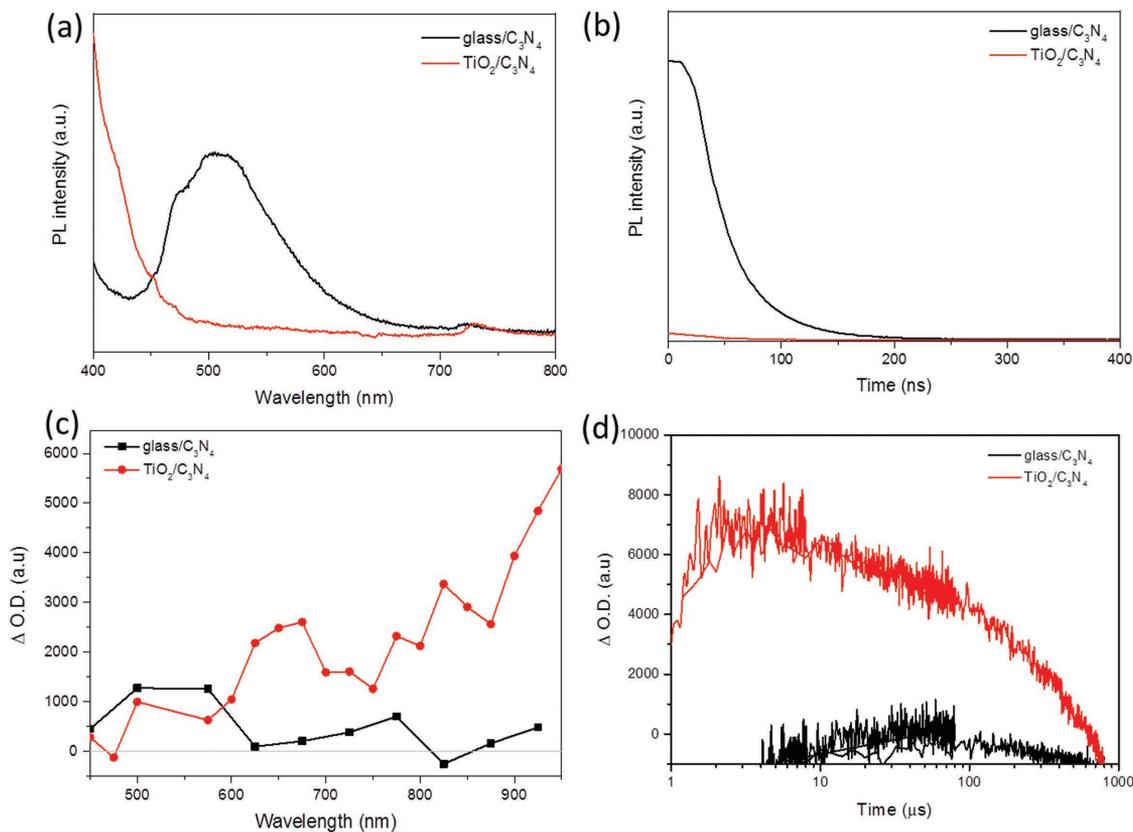


Figure 2. a) Emission spectra and b) emission temporal profile, monitored at 510 nm of glass/ C_3N_4 (black line) and $\text{TiO}_2/\text{C}_3\text{N}_4$ (red line) thin films upon excitation at 366 nm (see Figure S3, Supporting Information, for normalized spectra), c) transient spectra of glass/ C_3N_4 and $\text{TiO}_2/\text{C}_3\text{N}_4$ thin films acquired at 50 μs upon 532 nm excitation, and d) transient decays of glass/ C_3N_4 and TiO_2 monitored at 925 nm upon excitation at 532 nm.

light excitation. The emission decay of glass/C₃N₄ was fitted to a single exponential decay where a half-lifetime of 40 ns was obtained. The emission kinetics for TiO₂/C₃N₄ was found faster than our instrument response (≈ 1 ns). Therefore, efficient charge injection between the C₃N₄ excited states and the TiO₂ conduction band is expected since charge injection has been determined to be faster than radiative deactivation (40 ns).

In order to study the recombination processes, L-TAS experiments were carried out on C₃N₄ coated mesoporous TiO₂ thin films, and C₃N₄ directly grown on glass as a reference. Photoinduced charge transfer from the C₃N₄ excited states to the TiO₂ conduction band was established from the transient spectrum acquired at 50 μ s (Figure 1, Path 2) after 535 nm laser excitation, presenting a band increasing in absorptivity from ≈ 600 nm toward the NIR, as shown in Figure 2c. The transient absorption has been attributed to oxidized species in the C₃N₄. In order to confirm this proposal, spectroelectrochemical measurements were carried out (Figure S5, Supporting Information). In these experiments the UV-vis spectrum of a C₃N₄/TiO₂ electrode has been recorded before and after positive bias was applied. The absorption spectrum changed upon positive bias, appearing a band growing in intensity from 600 nm toward the NIR. In addition, this electrochemical oxidation was found reversible and negative bias restored the absorption spectrum to the initial features, subsequent cycling with positive bias promoting again NIR absorption.

For comparison purposes the transient spectrum of C₃N₄ deposited onto glass was also measured, showing negligible signal, indicating that the transient signal originates from the photoinduced electron transfer and not due to deactivation of the C₃N₄ excited states. On the other hand, the recombination kinetics in the TiO₂/C₃N₄ thin films was also investigated (Figure 2d). The electron recombination from the TiO₂ conduction band to the C₃N₄ valence band (Figure 1, Path 4) was found to occur with a half-lifetime of 200 μ s, presenting dispersive recombination dynamics as reported in other mesoscopic photovoltaic devices.^[27,28] This dispersive recombination dynamics is widely accepted to indicate “random walk” of electrons in mesoporous TiO₂ films in dye sensitized solar cells as well as in other semiconductor materials deposited on TiO₂ electrodes.^[29] The TiO₂/C₃N₄ decay data was fitted to a stretch exponential function (Equation (1)) and a lifetime (τ) of 197 μ s and β factor, which is related with the dispersion degree in the system ($0 < \beta < 1$), of 0.84

$$f(t) = A \cdot \exp\left[-(t/\tau)^\beta\right] \quad (1)$$

From the L-TAS measurements it can be estimated that the charge recombination between C₃N₄ and TiO₂ is three magnitude orders slower than charge injection in these electrodes, indicating favorable electron transfer kinetics between these competitive processes. Consequently, one can safely conclude that the charge separation between the TiO₂ and C₃N₄ is not the limiting factor of the cell efficiency. Further, the hole transfer process between the oxidized states in C₃N₄ and different electrolytes were also studied (Figure 1, Path 3). Liquid electrolytes based on I⁻/I₃⁻ and sulfide redox pairs, and solid state hole conductors including 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) and

poly(3-hexylthiophene) (P3HT) were used. L-TAS decay of TiO₂/C₃N₄ electrode shows that in the presence of I⁻/I₃⁻-based electrolyte the transient absorption signal (Figure 3a) dramatically quenched. This behavior is not surprising since the presence of this redox pair has usually produced quenching of the L-TAS signal at long time ranges in dye sensitized solar cells, due to the efficient disappearance of the oxidized species.^[30] In this case, there is a significant decrease in the signal intensity, although it can be still observed a long positive signal in the transient decay (Figure 3a). This can indicate that the oxidized species in C₃N₄ has been efficiently reduced by the I⁻/I₃⁻. Nevertheless, it has been previously reported that I⁻/I₃⁻ species are highly reactive with other metal-based semiconductor light harvesters such as quantum dots.^[31,32] Therefore, corrosion of the C₃N₄ cannot be discarded as the responsible of the transient signal quenching.

In the case of polysulfide-based electrolyte, the lifetime of oxidized species in C₃N₄ was reduced to 140 μ s. Due to the similar time range where charge recombination and hole extraction take place, it is reasonable that the obtained photocurrent in C₃N₄/TiO₂ PEC using this redox couple in the electrolyte was not as high as expected.^[26]

For the measurement of the solid hole conductor, spiro-OMeTAD, the electrolyte was deposited by spin coating on top of the TiO₂/C₃N₄ electrodes. Consequently, the L-TAS signal was significantly reduced, indicating efficient hole transfer from the oxidized C₃N₄ to the spiro-OMeTAD (Figure 3a). However, in the case of solid electrolyte, beside the hole extraction life time, suitable electrode configuration and adequate impregnation of the solid electrolyte molecules into the mesoporous network are needed to be optimized in order to achieve an efficient solar cell. Actually, it has been reported that these hole conductors are only able to diffuse 2–4 μ m in the mesoporous network and nanoparticles of 40 nm are required to produce big pores in the network to improve spiro-OMeTAD diffusion.^[33] Nowadays, there is ongoing research in our lab on finding the optimal cell configuration with a solid state electrolyte. The semiconductor P3HT polymer was also used as a hole conductor and it was spin coated onto the TiO₂/C₃N₄ substrate followed by annealing at 140 °C for 15 min. Surprisingly, the L-TAS showed enhanced transient signal in the region from 750 to 925 nm (Figure 3b). In addition, slower transient absorption kinetics were found in P3HT coated TiO₂/C₃N₄ films compared with the noncoated films. In order to elucidate possible hole transfer from the oxidized C₃N₄ to the P3HT, L-TAS experiment was carried out on a P3HT coated glass/C₃N₄ electrode (Figure 3c). Interestingly, this coated electrode present no transient signal, indicating the absence of hole transfer between the C₃N₄ and the P3HT. For that reason the enhanced transient absorption signal recorded in P3HT/C₃N₄/TiO₂ films could be attributed to a contribution of the complementary charge transfer reaction from the P3HT to the TiO₂ to the one of the C₃N₄. The P3HT cation spectra have been previously reported before to correspond to a band centered at 1050 nm which starts from 750 nm.^[34] Therefore, the obtained L-TAS signal would correspond to the oxidized C₃N₄ plus the P3HT cation, indicating that both materials are injecting electrons into the TiO₂ conduction band. Moreover, the P3HT cation lifetime in mesoporous TiO₂ has been reported to be in the millisecond time scale,^[35] which agrees with the measured transient decay acquired at 925 nm.

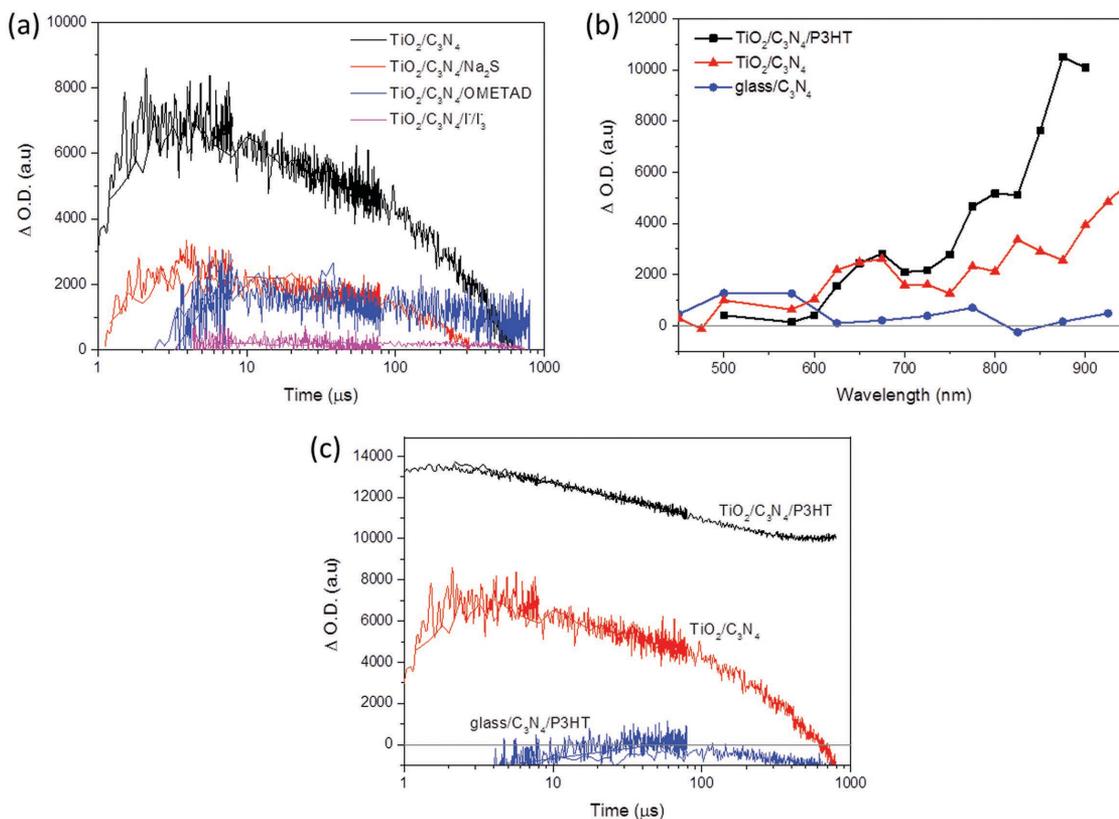


Figure 3. a) Transient decays of $\text{TiO}_2/\text{C}_3\text{N}_4$ electrodes in the presence of I^-/I_3^- and polysulfide-based liquid electrolytes and OMETAD solid electrolyte. The transient decays were monitored at 925 nm upon 532 nm excitation. b) Transient spectra of $\text{TiO}_2/\text{C}_3\text{N}_4$, glass/ C_3N_4 , and $\text{TiO}_2/\text{C}_3\text{N}_4/\text{P3HT}$ electrodes acquired at 50 μs upon 532 nm excitation and c) transient decay of the thin films monitored at 925 nm upon excitation at 532 nm.

In order to check the potentiality of C_3N_4 as photovoltaic material we have prepared mesoporous TiO_2 photoanodes sensitized with carbon nitride. Photoanode was checked using a redox electrolyte containing diiodine (I_2 0.03 M), lithium iodide (LiI 0.05 M) in methoxypropionitrile in three electrode configuration obtaining a modest photocurrent of $18.4 \mu\text{A cm}^{-2}$, indicating that the system is far away from an optimized configuration but showing also a photovoltaic effect. Currently, there is ongoing research in our lab to optimize the cell configuration including the electron acceptor layer and the hole mediators.

In conclusion, C_3N_4 has been proposed as a good candidate to act as light harvester material for photovoltaic devices. Charge injection and recombination have been proved to operate in optimum time ranges. However, the choice of a proper electrolyte together with the optimization of the electrode configuration still remain the main issues due to the poor regeneration characteristics presented by the typical liquid and solid hole conductors explored so far. We believe that a smart electrode design and the utilization of the right hole-transporter electrolytes will allow the implementation of C_3N_4 in many photoelectronic devices.

Supporting Information

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

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- [1] M. Gratzel, *Nature* **2001**, 414, 338.
- [2] P. V. Kamat, K. Tvrđy, D. R. Baker, J. G. Radich, *Chem. Rev.* **2010**, 110, 6664.
- [3] J. R. Durrant, S. A. Haque, E. Palomares, *Chem. Commun.* **2006**, 31, 3279.
- [4] J. H. Bang, P. V. Kamat, *Adv. Funct. Mater.* **2010**, 20, 1970.
- [5] S. Colodrero, A. Forneli, C. López, L. Pellejà, H. Míguez, E. Palomares, *Adv. Funct. Mater.* **2012**, 22, 1303.
- [6] S. A. Haque, Y. Tachibana, R. L. Willis, J. E. Moser, M. Grätzel, D. R. Klug, J. R. Durrant, *J. Phys. Chem. B* **2000**, 104, 538.
- [7] S. A. Haque, E. Palomares, B. M. Cho, A. N. Green, N. Hirata, D. R. Klug, J. R. Durrant, *J. Am. Chem. Soc.* **2005**, 127, 3456.
- [8] X. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.* **2009**, 8, 76.
- [9] X. C. Wang, K. Maeda, X. F. Chen, K. Takanabe, K. Domen, Y. D. Hou, X. Z. Fu, M. Antonietti, *J. Am. Chem. Soc.* **2009**, 131, 1680.
- [10] Y. Zheng, Y. Jiao, J. Chen, J. Liu, J. Liang, A. Du, W. Zhang, Z. Zhu, S. C. Smith, M. Jaroniec, G. Q. Lu, S. Z. Qiao, *J. Am. Chem. Soc.* **2011**, 133, 20116.

- [11] S. M. Lyth, Y. Nabee, S. Moriya, S. Kuroki, M. A. Kakimoto, J. I. Ozaki, S. Miyata, *J. Phys. Chem. C* **2009**, *113*, 20148.
- [12] J. Zhang, Y. Chen, X. Wang, *Energy Environ. Sci.* **2015**, *8*, 3902.
- [13] G. Zhang, Z. Lan, L. Lin, S. Lin, X. Wang, *Chem. Sci.* **2016**, *7*, 3062.
- [14] J. Xu, T. J. K. Brenner, Z. Chen, D. Neher, M. Antonietti, M. Shalom, *ACS Appl. Mater. Interfaces* **2014**, *6*, 16481.
- [15] Y. Wang, X. Wang, M. Antonietti, *Angew. Chem., Int. Ed.* **2012**, *51*, 68.
- [16] J. Xu, T. J. K. Brenner, L. Chabanne, D. Neher, M. Antonietti, M. Shalom, *J. Am. Chem. Soc.* **2014**, *136*, 13486.
- [17] J. Xu, M. Shalom, F. Piersimoni, M. Antonietti, D. Neher, T. J. K. Brenner, *Adv. Opt. Mater.* **2015**, *3*, 913.
- [18] B. Klahr, S. Gimenez, F. Fabregat-Santiago, T. Hamann, J. Bisquert, *J. Am. Chem. Soc.* **2012**, *134*, 4294.
- [19] W. Ma, D. Han, M. Zhou, H. Sun, L. Wang, X. Dong, L. Niu, *Chem. Sci.* **2014**, *5*, 3946.
- [20] J. Xiao, X. Zhang, Y. Li, *Int. J. Hydrogen Energy* **2015**, *40*, 9080.
- [21] J. Bian, J. Li, S. Kalytchuk, Y. Wang, Q. Li, T. C. Lau, T. A. Niehaus, A. L. Rogach, R. Q. Zhang, *ChemPhysChem* **2015**, *16*, 954.
- [22] J. Bian, L. Xi, C. Huang, K. M. Lange, R. Q. Zhang, M. Shalom, *Adv. Energy Mater.* **2016**, DOI: 10.1002/aenm.201600263.
- [23] J. Bian, Q. Li, C. Huang, J. Li, Y. Guo, M. Zaw, R. Q. Zhang, *Nano Energy* **2015**, *15*, 353.
- [24] J. Liu, H. Wang, Z. P. Chen, H. Moehwald, S. Fiechter, R. Van de Krol, L. Wen, L. Jiang, M. Antonietti, *Adv. Mater.* **2015**, *27*, 712.
- [25] J. Zhang, M. Zhang, L. Lin, X. Wang, *Angew. Chem., Int. Ed.* **2015**, *54*, 6297.
- [26] J. Xu, I. Herraiz-Cardona, X. Yang, S. Gimenez, M. Antonietti, M. Shalom, *Adv. Opt. Mater.* **2015**, *3*, 1052.
- [27] E. Palomares, J. N. Clifford, S. A. Haque, T. Lutz, J. R. Durrant, *J. Am. Chem. Soc.* **2003**, *125*, 475.
- [28] M. Ziolek, B. Cohen, X. Yang, L. Sun, M. Paulose, O. K. Varghese, C. A. Grimes, A. Douhal, *Phys. Chem. Chem. Phys.* **2012**, *14*, 2816.
- [29] J. Nelson, *Phys. Rev. B* **1999**, *59*, 15374.
- [30] A. Y. Anderson, P. R. F. Barnes, J. R. Durrant, B. C. O'Regan, *J. Phys. Chem. C* **2011**, *115*, 2439.
- [31] I. Mora-Seró, J. Bisquert, *J. Phys. Chem. Lett.* **2010**, *1*, 3046.
- [32] M. Shalom, S. Dor, S. Rühle, L. Grinis, A. Zaban, *J. Phys. Chem. C* **2009**, *113*, 3895.
- [33] I. K. Ding, N. Tétreault, J. Brillet, B. E. Hardin, E. H. Smith, S. J. Rosenthal, F. Sauvage, M. Grätzel, M. D. McGehee, *Adv. Funct. Mater.* **2009**, *19*, 2431.
- [34] H. Ohkita, S. Ito, *Polymer* **2011**, *52*, 4397.
- [35] Q. Tai, X. Zhao, F. Yan, *J. Mater. Chem.* **2010**, *20*, 7366.