Photo-induced electron transfer at nanostructured semiconductor-zinc porphyrin interface

Hanna Hakola^{*a}, Alexander Pyymaki Perros^b, Pasi Myllyperkiö^c, Kei Kurotobi^d, Harri Lipsanen^b, Hiroshi Imahori^{d,e}, Helge Lemmetyinen^a, and Nikolai V. Tkachenko^a

^aDepartment of Chemistry and Bioengineering, Tampere University of Technology, P.O. BOX 541, FI-33101 Tampere, Finland

^bDepartment of Micro- and Nanosciences, Aalto University, P.O. BOX 13500, FI-00076 Aalto, Finland

^cDepartment of Chemistry, University of Jyväskylä, P.O.BOX 35, FI-40014 University of Jyväskylä, Finland

^dInstitute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University Nishikyo-ku, Kyoto 615-8510, Japan

^eDepartment of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

* CORRESPONDING AUTHOR e-mail address: hanna.hakola@tut.fi

ABSTRACT Electron transfer at metal oxide-organic dye interface on ZnO nanorod (ZnOr) templates was studied by femtosecond absorption spectroscopy method. Further confirmation of the electron transfer was obtained from photoelectrical studies. The fastest electron transfer from zinc porphyrin (ZnP) to semiconductor was observed for ZnOr modified by a 5 nm layer of TiO₂ (<0.2 ps). The charge recombination processes were not affected by the TiO₂ being faster than at the interface of TiO₂ nanoparticle and ZnP. This indicates that the charge recombination depends mainly on semiconductor bulk properties whereas the charge separation is determined by the organic-semiconductor interface.

INTRODUCTION

Controlled surface functionalization and in-depth understanding of photoinduced processes at the organic dye-inorganic semiconductor interface are the key factors to improve the efficiency of photovoltaic devices.¹⁻⁴ Sensitizer-semiconductor interface in real devices is a complex object and the surface properties vary depending on multiple factors.⁴⁻⁵ Therefore the use of simplified model samples is essential to gain fundamental knowledge on electron transfer (ET) processes. So far, the major part of those samples consists of new organic photoactive molecules assembled on the film of commercial TiO₂ nanoparticles.⁶⁻¹⁰ These studies give valuable information for the design of the sensitizers. At the same time, the effect of semiconductors properties on the interfacial ET processes was widely discussed, though the key factors affecting the processes need better understanding.^{4,5,11}

ZnO has been considered as a good alternative to TiO₂ for photovoltaic applications.^{1,3,12-15} Bulk band gaps of ZnO and TiO₂ are similar, whereas ZnO has higher electron mobility than TiO₂. There are some advantages to use ZnO nanostructures in fundamental ET studies. Firstly, several fabrication methods are available and various controllable morphologies are possible to prepare. Secondly, Atomic Layer Deposition (ALD) is an accurate method to deposit additional layers of metal oxides (MO) conformally on ZnO nanostructures.^{14,15} The core-shell structures where the shell is prepared by ALD are promising materials for practical applications such as

photoanodes in dye sensitized solar cells (DSSC) or photoelectrochemical water splitting systems.¹⁴⁻¹⁸

The aim of this work was to study fundamental ET processes at metal oxide (MO) - organic dye interface. The samples were prepared using ZnO nanorods (ZnOr) as templates, covering them with a 5 nm layer of Al_2O_3 or TiO_2 and depositing zinc porphyrin (ZnP) photosensitizer layer on top of the MO nanostructures. Femtosecond transient absorption (TA) measurements were performed to study in detail the electron transfer kinetics from ZnP to MO. To link primary reactions at the sensitizer-semiconductor interface with real applications, the DSSC experiments were carried out using the same structures as in the TA study.

MATERIALS AND METHODS

Sample preparation The preparation of ZnOr substrates for spectroscopic measurements has been described in detail previously.¹⁹ Briefly, ZnOr were grown by hydrothermal method and were modified by growing a 5 nm thick layer of Al₂O₃ or TiO₂ by ALD. A 2 μm thick layer of TiO₂ nanoparticles (Solaronix: Ti-Nanoxide-T, denoted later as TiO₂p) was formed on the glass substrates by a standard doctor blading technique.¹⁰ 5-(4-Carboxyphenyl)-10,15,20-tris(2,4,6-trimethylphenyl)porphyrinatozinc(II) (ZnP) shown in Figure 1 was chosen as a sensitizer for this study.¹¹ The modified ZnO substrates and TiO₂p film were sensitized in a 0.2 mM ZnP in methanol at room temperature for one hour.¹⁰ Finally, the plates were rinsed thoroughly with methanol in order to remove all physisorbed ZnP molecules. The samples are denoted as ZnOr/ZnP, ZnOr/Al₂O₃/ZnP, ZnOr/TiO₂/ZnP and TiO₂p/ZnP later in the text.

The preparation of ZnOr on FTO substrates for the DSSC experiments was similar to that as described for ITO.¹⁹ The only difference was the number of spin coated ZnO seed layers. Two layers were required to ensure conformal ZnO seed layer on a rough FTO substrate. In addition to Al₂O₃ or TiO₂ modification layers, one set of ZnOr on FTO was modified by a 5 nm layer of ZnO. The FTO/ZnOr based electrodes were immersed into 0.2 mM ZnP in methanol for 24 hours and after the reaction rinsed carefully with pure solvent. Otherwise the DSSC samples were prepared as previously described.¹⁰

Sample characterization The morphology of ZnOr and TiO₂ nanoporous films were studied using a field emission scanning electron microscope (FE-SEM, Carl Zeiss Ultra 55). Absorption spectra were recorded by a Shimadzu UV-360 spectrophotometer. Steady state emission was measured by Fluorolog 3 fluorimeter using the correction function supplied by the manufacturer and all samples were excited at 430 nm. A time-correlated single-photon counting (TCSPC) system (PicoQuant GmbH) consisting of a PicoHarp controller and PDL-800-B driver was used for time-resolved fluorescence measurements. The samples were excited by a pulsed LED (LDH-P-C-405B) at 405 nm and fluorescence decays were monitored at 605 nm. Time resolution of the TCSPC measurements was approximately 60 – 70 ps (FWHM). The Fourier transform

infrared attenuated total reflectance (FT-IR-ATR) spectra were measured using a Perkin Elmer Spectrum One FT-IR Spectrometer equipped with a diamond crystal. The contact force between the sample and the crystal was kept the same for all samples and 64 scans were recorded with a resolution of 2 cm⁻¹.

For the transient absorption measurements, an integrated one-box femtosecond laser system (Integra-C 3.5 mJ, Quantronix) was used to pump two home-built non-collinear parametric amplifiers (NOPAs) delivering pump (560 nm) and probe (660 nm) pulses for the experiment. The detection of transient absorption was done using traditional two beam arrangement (probe and reference beams) giving a detection limit well below 0.1 mOD over 1000 shots. The mutual polarization of the pump and probe pulses was set to magic angle (54.7°). The time-resolution in the experiment was determined to be ~80 fs by sum-frequency cross-correlation signal generated in 0.1 mm thick BBO-crystal at the sample position. A fast (~100 fs) response was observed for all ZnO based samples regardless of TiO₂, Al₂O₃ or ZnP layers (Fig. S1) and is tentatively attributed to two-photon absorption in ZnO.²⁰ This fast response was subtracted from the sample signals shown below but it reduces the accuracy of measurements in a short time scale, <200 fs.

The photocurrent-voltage performances were measured with a solar simulator (PEC-L10, Peccell Technologies) providing AM 1.5 excitation spectrum (100 mW/cm²). The active area of the studied cell was 0.16 cm². Two cells of each sample type were measured and the average values are presented in the results.

Figure 1. Structure of studied zinc porphyrin, ZnP.

RESULTS AND DISCUSSION

Sensitization of nanorods Steady state absorption spectra of ZnP in methanol and ZnP SAMs on metal oxides are shown in Figure 2. The solution spectrum agrees well with the previous studies.¹⁰ The absorbances of ZnP SAMs on ZnOr, ZnOr/Al₂O₃ and ZnOr/TiO₂ are 0.3 - 0.7 at maxima, the Soret bands, and 0.02 - 0.04 at the strongest Q bands observed at around 550 nm. These absorbance values are in agreement with those of recently published for free base porphyrin SAMs on similar ZnOr and suggest reasonably high coverage of the semiconductor surfaces by ZnP.¹⁹ The variation in sample absorbances is mainly due to some differences in effective surface area of ZnOr templates (Fig. S2). In addition, the light scattering by the nanorods disturbs the measured spectra of ZnP SAMs especially in the Soret band region. Despite the spectrum of each particular substrate has been subtracted from the spectrum of its corresponding ZnP SAM sample, the quantitative comparison of the sample absorbances is rather inaccurate. Nevertheless, it is evident that TiO₂p/ZnP has significantly higher (approximately ten times) absorbance than that of ZnP SAMs on ZnOr substrates. This is directly related to the higher effective surface area of the 2 μ m thick mesoporous TiO₂p layer as compared to that of ZnOr (Fig S3).

Figure 2. Absorption spectra of ZnP in methanol (solid gray) and in the ZnOr/ZnP (short dot), TiO₂p/ZnP (dash), ZnOr/TiO₂/ZnP (solid black), and ZnOr/Al₂O₃/ZnP (dash dot) samples. Except TiO₂p/ZnP, all the spectra are multiplied by a factor of ten in the range 490-850 nm.

The binding mode of ZnP layer on semiconductors was studied by FT-IT-ATR spectroscopy method.^{9,21,22} The ATR spectra of a solid ZnP powder and ZnP bound to MO substrates are shown in supporting information (Fig. S4). The spectrum of solid ZnP has characteristic carboxylic acid stretching bands (C=O) and (C-O) at around 1700 and 1280 cm⁻¹, respectively. Upon binding these bands disappear and symmetric ((COO⁻)_{as}) and asymmetric ((COO⁻)_s) stretching bands of carboxylate groups appear at around 1400 and 1600 cm⁻¹. These characteristic features are observed when ZnP is bound to all studied substrates. The FT-IR-ATR signal intensity is not high in case of ZnOr based samples, but still a clear difference to the spectrum of solid unbound ZnP is found. The disappearance of strong (C=O) band in ZnP SAM spectra rules out the ester type binding mode and also indicates that no unbound ZnP is left on the metal oxide surfaces. The difference between the symmetric and asymmetric stretching bands of carboxylate group suggests bidentate binding mode of ZnP on all studied metal oxides.

Photoinduced electron transfer at the interface After photoexcitation, at least two states can be formed in the ZnP layer, the singlet excited state, ZnP^S, and the ZnP radical cation, ZnP^{•+}, which can be formed after the electron transfer from ZnP^S to the semiconductor.⁷ However, there are other possible deactivation reactions for ZnP^S, such as intermolecular interactions and enhanced non-radiative relaxations in the ZnP layer itself. Fluorescence spectra of ZnOr/ZnP, ZnOr/Al₂O₃/ZnP, and ZnOr/TiO₂/ZnP shown in Figure 3 illustrates a strong dependence of the fluorescence intensity on the semiconductor substrate. The fluorescence intensity is strongest for ZnOr/Al₂O₃/ZnP and most quenched for ZnOr/TiO₂/ZnP. This supports our hypothesis that the 5 nm layer of Al₂O₃ blocks the interactions between ZnP and ZnOr, leaving the intermolecular interactions in the ZnP layer as the major pathway for ZnP^S quenching. For other samples, the formation of ZnP^{•+} is the major reason for reduced fluorescence intensity.^{15,19} The measured average fluorescence lifetime for the ZnOr/Al₂O₃/ZnP is 0.34 ns, and in case of ZnOr/ZnP and

ZnOr/TiO₂/ZnP the lifetime is close to the TCSPC instrument resolution, being approximately 0.1 ns (Fig. S5). This also indicates that in the latter case the ZnP^S relaxation is strongly accelerated by interaction with the ZnO or TiO₂. The fluorescence of the TiO₂p/ZnP was quenched significantly stronger than that for ZnOr/TiO₂/ZnP and practically no signal was detected under otherwise identical measurement conditions. One reason for this can be increased intermolecular interactions. The probability of the dye-dye interactions in porous TiO₂p film can be high because the pore size is only few nanometers (Fig. S3).

Figure 3. Emission spectra of the ZnOr/Al₂O₃/ZnP (dash dotted) ZnOr/ZnP (short dot), and ZnOr/TiO₂/ZnP (solid) samples.

DSSC experiments provided another proof that Al₂O₃ layer suppress effectively the ZnP⁺ formation. The photocurrent-voltage characteristics are shown in Figure 4 and the performance parameters are summarized in Table 1. The efficiency of the ZnOr/Al₂O₃/ZnP solar cell is almost zero (= 0.001%). On the other hand, the ZnOr/ZnP, ZnOr/ZnO and ZnOr/TiO₂/ZnP cells have reasonable efficiencies compared to the low cell absorbances. Also for the same reason the photocurrent is roughly proportional to the cell absorption for all cells except of ZnOr/Al₂O₃/ZnP. The most remarkable differences between the ZnOr/ZnP or ZnOr/ZnO/ZnP and ZnOr/TiO₂/ZnP cells are found in U_{oc} and FF . Adding the TiO₂ layer on ZnOr increases the U_{oc} by 38% (from 0.39 V to 0.55 V) and FF by 60% (from 0.43 to 0.67).

Figure 4. IV- characteristics of studied samples based on ZnOr photoanodes.

Table 1. Photovoltaic properties of the samples and the absorption at the strongest Q band at 550 nm.

photoanode	J_{sc} (mA/cm ²)	U_{oc} (V)	FF	(%)	$A_{550\text{ nm}}$
ZnOr	1.0	0.40	0.42	0.17	0.060
ZnOr/ZnO	0.59	0.39	0.43	0.10	0.045
ZnOr/Al ₂ O ₃	0.01	0.24	0.43	0.001	0.030
ZnOr/TiO ₂	0.54	0.55	0.67	0.20	0.040

The most detailed information on photoinduced processes at MO-ZnP SAM interface was obtained from TA measurements. The preliminary experiments were carried out by acquiring spectra in the range 460-760 nm (see SI, Fig. S6) at varying the excitation densities. The aim was to find the excitation energy limit at which the signal decay profile does not depend on the excitation density. This study indicated that the sensitivity of the primary used system is not sufficient and another instrument optimized for detection of weak signals was used. However, this system is designed for TA decay measurements rather than for spectra studies. Therefore the most of the measurements were done with excitation at 560 nm and monitoring at 660 nm using 0.03 mJ/cm³ excitation density.

Although 660 nm is optimum wavelength for monitoring, ZnP^{*+} , ZnP^{S} state also has a contribution to the TA response at this wavelength.^{6-8,23} At first, with the excitation at 560 nm, the ZnP^{S} is populated and it gives an instant rise of the TA signal shown in Figure 5. The slower rise of the absorption at this wavelength can be attributed to the formation of ZnP^{*+} .⁶⁻⁸ The slower part of the rise was not observed for $\text{ZnOr}/\text{Al}_2\text{O}_3/\text{ZnP}$ sample, therefore there is no ET from ZnP to the semiconductor in this case. The analysis for the TA decays is not that straightforward, since the contributions of the ZnP^{S} and ZnP^{*+} cannot be separated. The decays of $\text{ZnOr}/\text{Al}_2\text{O}_3/\text{ZnP}$, $\text{ZnOr}/\text{TiO}_2/\text{ZnP}$ and ZnOr/ZnP look roughly the same (Figure 5 and Table 2). The signal intensities in TA responses were rather weak thus the accuracy of the calculated lifetimes shown in Table 2 is approximately 30 %. However, the TCSPC measurements show that at least at 100 ps delay time the population of ZnP^{S} of $\text{ZnOr}/\text{TiO}_2/\text{ZnP}$ and ZnOr/ZnP samples is much lower than that of $\text{ZnOr}/\text{Al}_2\text{O}_3/\text{ZnP}$; therefore the TA response of $\text{ZnOr}/\text{TiO}_2/\text{ZnP}$ and ZnOr/ZnP can be attributed to the decay of ZnP^{*+} . In addition, the DSSC measurements (Figure 4) suggest that the ET is very inefficient process in the case of $\text{ZnOr}/\text{Al}_2\text{O}_3/\text{ZnP}$. These three observations, the rise of absorption in subpicosecond time for $\text{ZnOr}/\text{TiO}_2/\text{ZnP}$ and ZnOr/ZnP only, much shorter fluorescence lifetime of the same samples and no photocurrent generation for $\text{ZnOr}/\text{Al}_2\text{O}_3/\text{ZnP}$, lead us to conclusion that origin of the transient absorption decays of these samples at 660 nm is different, although the lifetime is roughly the same. For $\text{ZnOr}/\text{TiO}_2/\text{ZnP}$ and ZnOr/ZnP the signal decay is mainly due to ZnP^{*+} , whereas in the case of $\text{ZnOr}/\text{Al}_2\text{O}_3/\text{ZnP}$ it arises from ZnP^{S} .

Figure 5. Transient absorption response of the ZnP SAMs on metal oxides. The signal intensity of TiO₂p/ZnP is divided by the factor of ten.

Table 2. Lifetimes and amplitudes of decay components obtained from transient absorption decays. τ_1 : formation of porphyrin radical cation, τ_2 and τ_3 : two decay time constants.

substrate	τ_1 rise	τ_2 decay	τ_3 decay
ZnOr	0.3 ps	50 ps [60%]	2.3 ns [40%]
ZnOr/TiO ₂	<0.2 ps, unresolved	50 ps [50%]	3.1 ns [50%]
ZnOr/Al ₂ O ₃	not formed	50 ps [60%]	2.5 ns [40%]
TiO ₂ p	0.9 ps	84 ps [20%]	> 2 ns [80%]

Transient absorption kinetics of TiO₂p/ZnP is in agreement with previous studies carried out in presence of 1:1 tert-butanol : acetonitrile.⁷ In our experiments carried out in air atmosphere, a clear rise of TA is seen for TiO₂p/ZnP with a time constant of 0.9 ps. At the ZnOr/ZnP interface, the ET is faster and takes place in a subpicosecond time domain (~0.3 ps). Even faster ET was observed for ZnOr/TiO₂/ZnP, but the time constant of the process interferes with the response of the ZnOr substrate and therefore can only be determined on a qualitative level to be <0.2 ps.

In part, these results are in contradiction with previous studies of ET dynamics on sensitized TiO_2 and ZnO nanoparticle thin films, which reported faster ET for TiO_2 than for ZnO.²⁴⁻²⁶ Comparison however is not straightforward to make because the sensitizers and nanostructures are different. Compared to TiO_2/ZnP , we observe faster ET not only for $\text{ZnOr}/\text{TiO}_2/\text{ZnP}$ but also for ZnOr/ZnP . This is a clear indication that the semiconductor nanostructure has a strong influence on the ET rate. The TiO_2 nanoparticle film is randomly packed and has grain boundaries and therefore electronic states differ from the bulk at every nanoparticle interface. On the contrary, one-dimensional ZnOr are single crystals with wurtzite structure and can provide a direct pathway for electron transport along the nanorods unlike the film of nanoparticles. Looking at only samples based on nanorods (ZnOr/ZnP and $\text{ZnOr}/\text{TiO}_2/\text{ZnP}$), TiO_2 enhances the ET rate. A 5 nm layer of TiO_2 may be too thin to have well defined crystal structure but is thick enough to change the electronic structure of the ZnOr surface.

The faster ET for TiO_2 than for ZnO can be attributed to differences in conduction band electronic structures of TiO_2 and ZnO.^{24,25} Although the band gaps of bulk ZnO and TiO_2 are very close to each other, TiO_2 has higher density of states than ZnO. This definitely is one reason for the faster ET rate, although in the case of sensitized ZnO nanorods and nanoparticle films the role of conduction band electronic structure in ET reaction rate has been under discussion.^{26,27} It has been suggested that ET proceeds via intermediate state at ZnO-sensitizer interface and this state is a major factor determining the ET rate. The intermediate state is related to ZnO properties because no stepwise ET is observed for the reference TiO_2 samples but its origin is still under intense study.^{26,27} Moreover, it is known that the ET at ZnP-semiconductor interface takes place through the space and is sensitive to the molecule arrangement on the surface and in particular to the tilt angle of ZnP.^{7,8,28} The surfaces of the semiconductors are heterogeneous and despite similar sensitizing conditions, variation in tilt angles as well as different types of porphyrin aggregates are possible. So far, the effect of these factors on the ET remain unclear since experimental determination of exact molecular organization on semiconductor surface is extremely challenging task.⁸

Although TiO_2 layer on ZnOr increases the ET rate, only a small difference in the charge recombination rate between the ZnOr/ZnP and ZnOr/ TiO_2 /ZnP is observed. Though the calculated longer lifetimes are somewhat different for these samples there is no visible difference in the decay profiles (Figure 5). The TiO_2 layer decreases slightly amplitude of ~50 ps decay component. One reason for this can be that the conductivity of the ZnOr core is higher than TiO_2 shell and the energy level of the conduction band of ZnO is slightly lower than that of TiO_2 .¹⁵ Therefore photoinjected electrons in ZnOr/ TiO_2 /dye structures move across the TiO_2 layer into ZnOr and the recombination rate is mainly determined by ZnOr. Among all measured samples, the charge recombination is slowest in TiO_2 p/ZnP. One possible explanation can be that the bulk carrier mobility of ZnO and TiO_2 contributes to the rate of charge recombination – the faster charge migration in ZnO makes charge recombination faster. The latter should not have a negative effect on the solar cell performance, since the higher carrier mobility is also beneficial for the efficient charge transport to the external circuit.

CONCLUSIONS

For both ZnOr/ZnP and ZnOr/ TiO_2 /ZnP interfaces the ET is efficient and fast, being faster than that at the interface of TiO_2 p/ZnP. A 5 nm thick TiO_2 shell on ZnOr modifies the surface electronic properties thus enabling sub-ps (<0.2 ps) ET reaction. The transient absorption measurements revealed only minor differences in the charge recombination rate between the ZnOr based samples but a clear difference is found in DSSC experiments. TiO_2 shell decreases the charge recombination as indicated by the increased open circuit voltage of the cell.

ACKNOWLEDGMENT

H.H. is grateful to doctoral program of the President of the Tampere University of Technology for the financial support. H. I., N. T., H. L., and H. H. thank Strategic Japanese-Finish Cooperative Program (JST, Tekes, and AF). The authors are grateful for Optoelectronics Research Centre (Tampere University of Technology) for SEM facilities. We also acknowledge the provision of ALD facilities by Aalto University at Micronova Nanofabrication Centre.

REFERENCES

1. J.A. Anta, E Guille- n, R. Tena-Zaera, J. Phys. Chem. C 116 (2012) 11413
2. A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chem. Rev. 110 (2010) 6595
3. Q. Zhang, C.S. Dandeneau, X. Zhou, G. Cao, Adv. Mater. 21 (2009) 4087
4. A. Listorti, B. O'Regan, J.R. Durrant, Chem. Mater. 23 (2011) 3381
5. O.V. Prezhdo, W.R. Duncan, V.V. Prezhdo, Prog. Surf. Sci. 84 (2009) 30
6. A.S. Hart, C.B. KC, H.B. Gobeze, L.R. Sequeira, F. D'Souza, ACS Appl. Mater. Interfaces 5 (2013) 5314
7. H. Imahori, S. Kang, H. Hayashi, M. Haruta, H. Kurata, S. Isoda, S.E. Canton, Y. Infahsaeng, A. Kathiravan, T. Pascher, P. Chabera, A.P. Yartsev, V.J. Sundström, J. Phys. Chem. A 115 (2011) 3679
8. S. Ye, A. Kathiravan, H. Hayashi, Y. Tong, Y. Infahsaeng, P. Chabera, T. Pascher, A.P. Yartsev, S. Isoda, H. Imahori, V.J. Sundström, J. Phys. Chem. C 117 (2013) 6066
9. H. Imahori, S. Hayashi, H. Hayashi, A. Oguro, S. Eu, T. Umeyama, Y. Matano, J. Phys. Chem. C 113 (2009) 18406
10. H. Imahori, Y. Matsubara, H. Iijima, T. Umeyama, Y. Matano, S. Ito, M. Niemi, N.V. Tkachenko, H.J. Lemmetyinen, J. Phys. Chem. C 114 (2010) 10656
11. H. Imahori, S. Hayashi, T. Umeyama, S. Eu, A. Oguro, S. Kang, Y. Matano, T. Shishido, S. Ngamsinlapasathian, S. Yoshikawa, Langmuir 22 (2006) 11405

12. T. Ling, J.-G. Song, X.-Y. Chen, J. Yang, S.-Z. Qiao, X.-W. Du, *J. Alloys Compd.* 546 (2013) 307
13. M. McCune, W. Zhang, Y. Deng, *Nano Lett.* 12 (2012) 3656
14. O. Lupan, V.M. Guérin, I.M. Tiginyanu, V.V. Ursaki, L. Chow, H. Heinrich, T. Pauporté, *J. Photochem. Photobiol., A* 211 (2010) 65
15. M. Law, L.M. Greene, A. Radenovic, T. Kuykendall, J. Liphardt, P.J. Yang, *J. Phys. Chem. B* 110 (2006) 22652
16. M. Liu, C.-Y. Nam, C.T. Black, J. Kamcev, L. Zhang, *J. Phys. Chem. C* 117 (2013) 13396
17. A.K. Chandiran, P. Comte, R. Humphry-Baker, F. Kessler, C. Yi, M.K. Nazeeruddin, M. Grätzel, *Adv. Funct. Mater.* 23 (2013) 2775
18. V.O. Williams, N.C. Jeong, C. Prasittichai, O.K. Farha, M.J. Pellin, J.T. Hupp, *ACS Nano* 6 (2012) 6185
19. H. Saarenpää, E. Sariola-Leikas, A. Pyymäki Perros, J. Kontio, A. Efimov, H. Hayashi, H. Lipsanen, H. Imahori, H. Lemmetyinen, N.V. Tkachenko, *J. Phys. Chem. C*, 116 (2012) 2336
20. R.J. Ellingson, J.L. Blackburn, J. Nedeljkovic, G. Rumbles, M. Jones, H. Fu, A.J. Nozik, *J. Phys. Rev. B* 67 (2003) 075308
21. M.K. Nazeeruddin, R. Humphry-Baker, D.L. Officer, W.M. Campbell, A.K. Burrell, M. Grätzel, *Langmuir* 20 (2004) 6514
22. J. Rochford, E. Galoppini, *Langmuir* 24 (2008) 5366
23. Z. Gasyna, W.R. Browett, M.J. Stillman, *Inorg. Chem.* 24 (1985) 2440
24. J.B. Asbury, E. Hao, Y. Wang, H.N. Ghosh, T.J. Lian, *J. Phys. Chem. B*. 105 (2001) 4545
25. V. Thavasi, V. Renugopalakrishnan, R. Jose, S. Ramakrishna, *Mat. Sci. Eng. R* 63 (2009) 81
26. H. Nímc, J. Rochford, O. Taratula, E. Galoppini, P. Kužel, T. Polívka, A. Yartsev, V. Sundström, *Phys. Rev. Lett.* 104 (2010) 197401

27. C. Strothkämper, A.F. Bartelt, P. Sippel, T. Hannappel, R. Schuetz, R.J. Eichberger, *Phys. Chem. C* 117 (2013) 17901
28. M. Niskanen, M. Kuisma, O. Cramariuc, V. Golovanov, T.I. Hukka, N. Tkachenko and T.T. Rantala, *Phys. Chem. Chem. Phys.* 15 (2013) 17408.

Electron
transfer
< 0.2 ps