Hybrid dye-metal oxide nanoparticles for superior low-temperature dye-sensitized solar cells

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A. Kunzmann,^a S. Valero,^b A. E. Sepúlveda,^c M. Rico,^{b,d} E. Lalinde,^c J. R. Berenguer,^c J. García-Martínez,^b D. M. Guldi,^a E. Serrano,^{b*} and R. D. Costa^{a*}

This work reports on a new strategy to design low-temperature ($\leq 200^\circ\text{C}$) sintered dye-sensitized solar cells (It-DSSCs) with enhanced charge collection efficiencies (η_{coll}), photoconversion efficiencies, and stabilities under continuous operation conditions. This is accomplished by integrating into the electrodes a new class of hybrid mesoporous Ru(II) complex-TiO₂ nanoparticles (TiO₂-Ru-IS), obtained by *in-situ* bottom-up construction of dye-sensitized titania using the Ru(II) N3 dye as building blocks. The most important assets of the TiO₂-Ru-IS hybrid nanoparticles are i) a remarkable dye stability due to the integration of the dye within the anatase network and ii) a small nanoparticle size to enhance charge transport/collection processes. The latter is encouraging for tackling the two main bottlenecks in It-DSSCs, that is, moderate efficiencies and low device stabilities. Our results evidence that devices with electrodes featuring a mixture of P25 and TiO₂-Ru-IS show an enhanced charge transport and reduced electron recombination processes. The incorporation of TiO₂-Ru-IS into the electrode leads to an increase of η_{coll} from 46% for P25 reference up to 60% for P25:TiO₂-Ru-IS (80:20 wt%) device. As a final optimization, TiO₂-Ru-IS was also applied as a top layer in a multi-layered device architecture, leading to η_{coll} of around 74%. The latter result in It-DSSCs featuring efficiencies of 8.75% and lifetimes of 600 h under device operation conditions.

Introduction

During the last decade, dye-sensitized solar cells (DSSC) have been established as a low-cost alternative to conventional silicon-based solar cells due to their high photoconversion efficiency and easy manufacturing as well as recycling.¹⁻⁵ In addition, the device efficiency is nearly independent of the working conditions, providing a more stable power output during the course of days. Indeed, DSSC modules tested under real-world conditions show efficiencies of around 7.5%, while accelerated ageing tests indicate that they potentially feature lifetimes of 40 and 25 years for Middle European and South European conditions, respectively.⁶⁻¹¹

However, to implement DSSCs at industrial scale some persisting problems need to be addressed. Firstly, the sintering temperatures for the semiconducting electrode need to be significantly lower than the 450–500 °C usually employed for DSSC fabrication.^{1-8, 12-14} As a matter of fact, if a suitable low-temperature annealing material and process is developed, an inexpensive but low-heat-resistant transparent conductive oxide (TCO) glass substrate, as well as plastic substrates, could

be used for low temperature DSSC (It-DSSCs) manufacturing. The latter would significantly lower the production costs and dramatically increase the application versatility of It-DSSCs. However, low sintering temperatures usually lead to an inefficient interconnection between the nanoparticles, resulting in poor charge transport and charge collection features leading to greatly reduced device efficiencies.¹¹⁻²⁶ Secondly, long term device stability is still missing, making large scale applicability of It-DSSCs problematic. This is related to prominent dye degradation through interactions with the electrolyte and desorption of the dye from the surface under operation conditions which constitutes the second main bottleneck of It-DSSCs.^{20-23, 27-32}

To tackle the first challenge – *i.e.* to reduce the sintering temperatures while improving the nanoparticle interconnection – multiple strategies have been proposed in literature. The most promising approaches include, i) binder-free pastes,³³⁻³⁵ ii) the compression treatment,³⁶⁻⁴¹ iii) spray and/or electrophoretic depositions,⁴²⁻⁴⁴ iv) lift-off transfer technique,⁴⁵ v) the use of a polymer composite matrix,^{46,47} and vi) interconnected nanoparticle-embedded microbead-type TiO₂.^{48,49} The resulting efficiencies have been moderate, usually ranging between 4–7%,^{11,33-49} while the highest efficiency of 8.1% was reported by Yamaguchi *et al.* in 2010.³⁸ Among these examples, only low efficient devices showed half-life times of around 1,000 h at best.^{11,33-49} To circumvent this problem, several strategies have been explored in order to protect the dye.

^a Department of Chemistry and Pharmacy, University of Erlangen-Nuremberg (FAU), Egerlandstr. 3, D-91058 Erlangen, Germany. E-mail: ruben.costa@fau.de

^b Laboratorio de Nanotecnología Molecular, Departamento de Química Inorgánica, Universidad de Alicante, Ap. 99, E-03080 Alicante, Spain. URL: www.nanomol.es. Email: elena.serrano@ua.es. orcid.org/0000-0003-3340-6675

^c Departamento de Química-Centro de Investigación en Síntesis Química (CISQ), Universidad de La Rioja Madre de Dios, 54, E-26006, Logroño, La Rioja, Spain. Electronic Supplementary Information (ESI) available: Device characterization by means of J-V curves, EIS, and over time is provided. See DOI: 10.1039/x0xx00000x

Fig 1. Top: Schematic synthesis of the hybrid Ru(II) complex-titania (TiO₂_Ru_IS), including pictures of TiO₂_Ru_IS and the non-hybrid (NH) nanoparticle powder. Adapted from ref. 53. Bottom: Schematic representation of electrode architecture developed in this work, single layer and multi layered electrodes, with different configurations.

For example, i) the use of additives in the electrolyte,^{24, 25} ii) the stabilization of dye binding by using an atomic layer deposition approach,²⁴⁻²⁶ and iii) the development of *quasi*-solid state or solid-state electrolytes.⁵⁰⁻⁵¹ However, the use of low temperature sintering methods aimed at significantly extending at the same time, the lifetime and the efficiency of the device has been challenging up to date.

Herein, a new approach is proposed to enhance both, charge collection efficiency and device lifetime, realizing highly efficient and stable It-DSSCs. In short, we demonstrate how to combine non hybrid TiO₂-based nanoparticles (NH; 8 nm), commercially available P25 TiO₂, and a newly developed dye-hybrid TiO₂ nanoparticles (TiO₂_Ru_IS; 8 nm),^{52,53} in which the Ru(II) N3 dye is incorporated into the structure of the titania nanoparticle, to fabricate single, and/or multi-layered electrodes for superior It-DSSCs (see Fig. 1). The hybrid TiO₂_Ru_IS nanoparticles are prepared by using a recently reported one-pot co-condensation “Sol-Gel Coordination Chemistry” strategy, based on the *in-situ* co-condensation of a titania precursor and adequately functionalized organic or coordination dyes. Particularly, the reaction between the Ru(II) N3 dye and Ti(IV) tert-butoxide (TBOT) leads to a bimetallic Ru(II)-titanium complex with alkoxide terminal groups, which

after hydrolysis, produces a gel with the dye homogeneously incorporated in the titania gel network (see Fig. 1). The dye content can be conveniently adjusted by controlling the dye/TBOT ratio. Upon further condensation at room temperature and low temperature crystallization, anatase nanoparticles (see Fig. 1 and S1, ESI) containing the Ru(II) N3 dye inside them are obtained.⁵²⁻⁵⁵

Two aspects constitute the major thrust of this work. Firstly, devices with electrodes featuring a mixture of P25 and small nanoparticles show an increase of the device efficiency due to an enhanced interconnection between nanoparticles. Secondly, the use of TiO₂_Ru_IS nanoparticles enhances the charge collection efficiency and stability. Importantly, the integration of the Ru(II) dye N3 into the structure of the anatase – better than that obtained by traditional post-synthetic methods – produces changes in the electronic properties of the crystalline titania, decreasing its band gap up to 2.82 eV – enhancing injection from the surface bound dyes –, and also it acts as a dye itself (Fig. S1, ESI).^{52,53} In addition, the integration of the dye in the titania structure protects the electrode against electrolyte corrosion due to the significantly reduction of the electron recombination process.

Based on the latter assets, we firstly report on the influence of $\text{TiO}_2\text{-Ru-IS}$ within the electrode and determine the best device production parameters – *i.e.* temperature and particle ratios – providing a comprehensive study using electrochemical impedance spectroscopy (EIS). Next, we prove that the use of P25 as bottom layer and $\text{TiO}_2\text{-Ru-IS}$ as top layer leads to device stabilities of over 1,000 h. Finally, we show that devices with multi-layered electrodes combining P25 and NH as bottom layer and $\text{TiO}_2\text{-Ru-IS}$ as top layer features charge collection efficiencies (η_{coll}) of 74%, remarkable device efficiencies of 8.75% and that are stable up to 600 h under operation conditions. The latter represents a nearly four-fold increase in efficiency and stability with respect to our reference *It*-DSSCs based on P25 nanoparticles, as well as the highest efficiency value reported for *It*-DSSCs up to date.¹¹ These notions are monitored and validated by means of photocurrent-voltage (*J*-*V*) and EIS assays in both short and long time endurance tests. In general terms, our approach shows for the first time how to manufacture highly stable and remarkably efficient *It*-DSSCs taking the advantage of novel hybrid dye- TiO_2 nanoparticles prepared by the incorporation of the Ru(II) dye into the titania structure during their synthesis. Additionally, this approach might be applicable to any kind of dyes allowing for tuneable light absorption features of the device, while still retaining exceedingly high lifetimes and efficiencies.⁵²⁻⁵³

Results and discussion

Low-temperature DSSCs based on P25: $\text{TiO}_2\text{-Ru-IS}$ electrodes.

As a first step towards the preparation of *It*-DSSCs, we followed previous works investigating the optimal amount of hydrochloric acid (HCl) as nanoparticle binder with commercial P25 titania to fabricate reference devices – see Experimental Section for details.^{33-35,56-60} Six pastes were prepared with HCl in concentrations ranging from 0.5 to 5.5 M, doctor bladed onto fluorine doped tin-oxide (FTO) substrates, and heated to 200 °C for 30 minutes to remove the solvent. Here, HCl modifies the nanoparticle surface by increasing the number of hydroxyl groups, which during sintering form Ti-O-Ti connections between nanoparticles. This procedure enables *ca.* 10 μm thick electrodes, which were immersed at 80 °C into a ruthenium-based dye solution and, subsequently, used as working electrodes in conjunction with platinum-based counter electrodes and an iodine-based electrolyte – see Experimental Section for details. The figures-of-merit and representative *J*-*V* curves are displayed in Fig. S2, ESI. In short, devices prepared with a 1 M HCl paste outperform any other, featuring an efficiency (η) of 2.3%, a short-circuit current density (J_{sc}) of 3.9 mA/cm^2 , an open-circuit voltage (V_{oc}) of 0.79 V, and a fill factor (FF) of 74%. Notably, all devices have remarkable V_{oc} s of around 0.8 V, and FFs of over 70%, pointing to an optimum device fabrication. The only change upon variation of the HCl concentration stems from the changes in J_{sc} s (Fig. S2, ESI). This finding might relate to the impact that the amount of HCl has on the charge transport due to the interconnection between nanoparticles. For instance, although an optimization with HCl has been successfully performed, the charge collection efficiencies (η_{coll}) of the best device is with 46% still moderate.

As such, a better charge transport and lower recombination processes is still needed. As already outlined, the modification of the electrodes by implementing, for example, nanocarbons, metals, or small nanoparticles is one of the most promising strategies to enhance the η_{coll} values.^{1-5,56,57} Here, the size of $\text{TiO}_2\text{-Ru-IS}$ nanoparticles with 8 nm renders them as suitable candidates, especially in comparison to a size of 25 nm for P25. As such, $\text{TiO}_2\text{-Ru-IS}$ and P25 were mixed at different mass ratios going from 100:0 (pure P25) to 0:100 (pure $\text{TiO}_2\text{-Ru-IS}$). The P25: $\text{TiO}_2\text{-Ru-IS}$ electrodes were sintered following the above-described procedure, *i.e.* at 200°C, 30 min. Importantly, thermogravimetric analysis (TGA) and steady-state absorption corroborated the stability of the hybrid during the sintering process (Fig. S3, ESI).

The morphology of the electrodes was investigated by using scanning electron microscopy (SEM). Fig. 2a documents that the implementation of the hybrids has a significant effect on the electrode morphology. While pure P25 shows a porous morphology based on individualized nanoparticles, the 80:20 (P25: $\text{TiO}_2\text{-Ru-IS}$) electrodes show a seemingly well-interconnected structure. Going, however, beyond this hybrid content, the film morphology changes, showing rather homogenous cluster formations, which strongly reduce the porosity of the films. To confirm this finding, the roughness average was determined by three approaches, namely dye desorption studies, profilometry measurements, and diffuse reflectance (DR) measurements (Fig. 2b-d). From the first approach, the roughness parameter (*R*) is derived by considering the amount of dye adsorbed onto the electrode – see Experimental Section for details.^{60,61} As shown in Fig. 2b, *R* is almost constant followed by a linear decrease upon increasing the amount of hybrid materials to more than 20 wt%. This is also corroborated by the roughness average calculated with profilometry measurements (Fig. 2c). Here, the values, which were derived from a Gaussian fitting of the surface profile, indicate that small amounts of $\text{TiO}_2\text{-Ru-IS}$ ($\geq 20\%$) slightly reduce the roughness compared to that of the pure P25 electrode, while large $\text{TiO}_2\text{-Ru-IS}$ amounts have a profound impact on the roughness. Finally, the DR value at 410 nm is significantly reduced upon increasing the amount of $\text{TiO}_2\text{-Ru-IS}$ nanoparticles (Fig. 2d).

Next, *It*-DSSCs based on P25: $\text{TiO}_2\text{-Ru-IS}$ electrodes with different composition were fabricated and tested under simulated 1,000 W/cm^2 AM 1.5 illumination (Fig. 3a). Table S1, ESI and Fig. 3b-c summarizes the photovoltaic performances of these devices. A direct comparison of the device performance shows a clear trend. Here, the increase of $\text{TiO}_2\text{-Ru-IS}$ in the electrode with values of up to 20 wt% does not affect V_{oc} , but significantly enhances J_{sc} , reaching a maximum efficiency of around 4% (Fig. 3b-c and Table S1, ESI). This is attributed to superior charge collection features due to a better interconnection between individual nanoparticles. Beyond 20 wt% of $\text{TiO}_2\text{-Ru-IS}$, all the figures-of-merit start to decline. Based on the electrode characterization, this relates to a lower dye uptake due to a lower *R* of the electrode morphology as corroborated in the SEM assays (Fig. 2a).

Fig 2. (a) SEM images of P25:TiO₂_Ru_IS electrodes with a mass ratio of 100:0, 80:20, 50:50 and 0:100, respectively. (b-d) Relative changes in roughness values (R) calculated by means of desorption studies (b) and *via* profilometry measurements (c) using the pure P25 electrode as a reference, as well as light scattering spectra of the electrodes with increasing amounts of TiO₂_Ru_IS in the electrodes (d).

The latter reduces the density of injected charges in the electrode and hamper the charge transport, since the cluster domain boundaries might act as efficient charge recombination centres.

EIS measurements were performed under dark and illumination conditions to characterize the charge transport and recombination processes. These analyses were conducted based on the equivalent circuit model shown in Fig. S4, ESI and the key parameters are summarized in Table S1, ESI. As shown in Fig. 3f and Fig. S4, ESI, the Nyquist plots are best described as two semicircles. On one hand, the feature in the high frequency range is attributed to the electrolyte regeneration at the platinum/electrolyte interface and is located in the kHz domain. On the other hand, the one in the low frequency range (1-100 Hz) correlates with electron transfer processes across the electrode/dye/electrolyte interface. The diameter of the latter semicircle is a consequence of balancing charge transport and charge recombination. Under illumination, the resistance towards charge transport (R_w) at the semiconducting network dominates, while under dark conditions the electron back reaction from the electrode to the electrolyte, that is, the resistance to recombination (R_k), takes over. The interplay between these parameters is best seen when η_{coll} is analysed.

The latter is used to assess the quality of the electrode under operation conditions.

A comparison of the EIS results upon increasing the amount of TiO₂_Ru_IS in the electrode points to two findings. Studies under dark conditions showed that the low-frequency semicircle diminishes initially when TiO₂_Ru_IS is present and stays at low values for devices with 50:50 P25:TiO₂_Ru_IS electrode (Fig. S4, ESI). This indicates increased interfacial recombination of electrons due to low R_k .

Under illumination conditions, the same semicircle is significantly reduced and shifted to lower frequencies. This is an indication for an R_w decrease, but only until devices with 70:30 electrodes (Fig. 3e). From there on, the diameters of the semicircle begin to increase again, indicating that the charge transport declines (Fig. 3f). Upon closer inspecting the electron lifetime (τ) changes, the different R_w s and R_k s are rationalized on the basis of charge trapping, which is quite likely related to the cluster formations – *vide supra*. When the TiO₂_Ru_IS content ranges from 20 wt% to 50 wt%, electron transport throughout the electrodes is slightly hampered and R_w increases.

Fig 3. Photovoltaic performance and EIS analysis of the It-DSSCs prepared with P25:TiO₂-Ru-IS electrodes with different composition. (a) Schematic representation of the electrode setup, (b) J-V curves, (c) changes in photoconversion efficiency, and changes in EIS parameters – *i.e.*, τ and η_{coll} (d), R_w and R_k (e), as well as the corresponding Nyquist plots measured under illumination conditions (f).

At the same time, the electron recombination at the electrode/electrolyte interface increases. This is highlighted by the steady increase of τ , which maximizes for devices featuring TiO₂-Ru-IS amounts of 30 wt%, followed by a sudden reduction upon increasing the hybrid content (see Fig. 3d and Table S1, ESI). All of the aforementioned aspects concerning the ratio of the R_w/R_k values are reflected in the changes of η_{coll} . In particular, η_{coll} peaks for devices with 80:20 electrodes, substantiating the relationship between device efficiencies and η_{coll} upon increasing the TiO₂-Ru-IS content (Fig. 3c and Table S1, ESI). As such, electrodes featuring 20 wt% TiO₂-Ru-IS show the optimum balance between charge transport and recombination process under device operation conditions, enhancing by almost two-fold the device efficiency compared to the P25-based reference.

Although, the electrodes containing TiO₂-Ru-IS feature an increased efficiency compared to the P25 reference device, notable problems still persist. Indeed, while R_w is reduced when 80:20 mixtures are used compared to the reference (33 Ω vs. 150 Ω , respectively), the value itself remains high. This indicates

problems with the electron transport inside the electrode. To identify if the integration of the Ru dye into the structure of the titania nanoparticles leads to these downsides, non-hybrid (NH) TiO₂ nanoparticles prepared following the same procedure to that used for the hybrid TiO₂-Ru-IS and featuring the same nanoparticle size, were investigated for reference purposes.

To this end, devices with electrodes consisting of 80:20 wt% (P25:NH and TiO₂-Ru-IS) were compared under the same conditions. A schematic representation of the electrode composition is presented in Fig. 4a. The resulting J-V characteristics, the Nyquist plots, as well as long-term stability assays are displayed in Fig. 4b-e.

A direct comparison of the J-V measurements shows two clear trends (Fig. 4b). On one hand, the J_{sc} is vastly increased from 7 mA/cm² for the P25:NH device to 12 mA/cm² for the P25:TiO₂-Ru-IS devices, pointing to a successful enhancement of the electron transport capabilities of the electrodes. This suggests, that the incorporated dye disrupts the charge transport features.

Fig 4. Photovoltaic performance and Nyquist plots of the It-DSSCs prepared with either P25:TiO₂_Ru_IS (red solid line) or P25:NH (blue dotted line) electrodes, featuring a composition of 80:20 wt %, respectively. (a) Schematic representation of the electrode setup, (b) J-V curves, (c) the corresponding efficiency evolution over time, and comparison of the Nyquist plots under illumination (d) and in dark conditions (e).

On the other hand, the V_{oc} is reduced from 0.80 V for P25:TiO₂_Ru_IS devices to 0.66 V for P25:NH devices. The latter might be due to the protective effects of the TiO₂_Ru_IS nanoparticle layer, which prevents electron recombination and, indeed, reduces electronic interference of the electrolyte towards the semiconductor surface. However, even though the V_{oc} is lower, the gain in J_{sc} overcompensates the latter loss leading to an efficiency of the P25:NH device of *ca.* 5%, while the P25:TiO₂_Ru_IS cell features 4 %.

To provide a better understanding of these findings, EIS experiments were performed under dark and illumination conditions using the equivalent open circuit model shown in Fig. S4, ESI. As shown in Fig. 4d and 4e, the Nyquist plots are best described as two semicircles. A comparison of the EIS results confirms the above hypothesis. Under illumination conditions, the R_w value of devices with P25:TiO₂_Ru_IS is double compared to those noted for devices with P25:NH – 33 Ω and 19 Ω , respectively. The latter signifies a drastically increased electron

transport capability for electrodes featuring P25:NH, leading to better J_{sc} values (Fig. 4b). However, under dark conditions, the R_k values of P25: TiO₂_Ru_IS are much higher than those of P25:NH (81 Ω and 50 Ω , respectively), corroborating the underlying reasons for the intrinsically higher V_{oc} values for the former (Fig. 4b). This also points towards the fact, that the use of TiO₂_Ru_IS could indeed, electronically protect the electrode.

To further investigate these aspects, we fabricated bare NH and TiO₂_Ru_IS electrodes without dye sensitization and tested them under the same conditions (Fig. S5, ESI). Two findings were noted. IPCE and J-V analyses confirmed that the internal dye performs charge injection and, at the same time, prolongs the lifetime of the electrode against corrosion with the electrolyte. In other words, devices with electrodes prepared with TiO₂_Ru_IS nanoparticles are significantly more stable compared to traditional NH-based devices (Fig. S5, ESI).

Fig 5. Photovoltaic performance and EIS analysis of the It-DSSCs prepared with multilayered P25/ $\text{TiO}_2\text{-Ru_IS}$ electrodes with different configurations in comparison with the reference electrode (P25). (a) Schematic representation of the electrode setup, (b) figures-of-merit, (c) SEM image of half covered electrode featuring a hybrid $\text{TiO}_2\text{-Ru_IS}$ top layer, (d) J-V curves and (e) IPCE's of the devices.

In detail, after 200 h, no decrease in efficiency could be noted for $\text{TiO}_2\text{-Ru_IS}$ -based devices, while traditional ones showed an immediate drop in efficiency within the first 40 hours. Quite likely, this is related to the reduced charge recombination process due to the integration of the Ru(II) dye into the structure of the titania.

As such we can safely conclude that while the use of $\text{TiO}_2\text{-Ru_IS}$ leads to a loss of charge transport, it strongly increases both, the stability and the resistance towards recombination with the electrolyte. Indeed, this feature might be beneficial for further reduction of electron loss pathways when a layer of the $\text{TiO}_2\text{-Ru_IS}$ nanoparticles is applied on top of an efficient electrode.

As such, these novel dye- TiO_2 hybrid nanoparticles prepared by the integration of the Ru(II) dye into the anatase structure seem better suited for designing It-DSSCs with multi-layered architectures – see below.

Low-temperature DSSC based on multi-layered P25/ $\text{TiO}_2\text{-Ru_IS}$ electrodes.

To manufacture multi-layered electrodes, both pastes – *i.e.*, the reference P25 and the $\text{TiO}_2\text{-Ru_IS}$ paste – were subsequently doctor bladed on top of each other applying the later as bottom or top layer, leading to multi-layered electrodes, which were sintered at 200 °C for 30 min (Fig 5a). To ensure that after sintering the nature of the multi-layered electrode is not affected, we performed SEM assays with half covered electrodes (Fig. 5c). Although both layers are interconnected, the electrode preserves the multi-layered architecture upon sintering featuring a thickness of *ca.* 10 μm , being the morphology of each layer in sound agreement with the SEM results shown in Fig. 2 for P25 (100:0) and $\text{TiO}_2\text{-Ru_IS}$ (0:100) electrodes. Next, the devices were finalized as described above. The photovoltaic performance and EIS analysis of the It-DSSC based on multi-layered electrodes is summarized in Fig. 5.

Fig 6. Changes of the figures-of-merit (left) and the EIS parameters (right) of devices with a multi-layered electrode featuring a TiO_2 _Ru_IS top layer measured over time under operation conditions.

As expected from the poor charge transport features of the hybrid nanoparticles, the use of bottom hybrid layers leads to low V_{oc} s and J_{sc} s. In contrast, the use of top hybrid layers significantly enhances J_{sc} and slightly increases V_{oc} relative to the reference device (P25) leading to an increase of the efficiency up to values of 5.4% (Fig. 5b and d). Based on the aforementioned features of the hybrid layers, we postulate that the increase in J_{sc} and η relates to the reduction of the electron recombination processes, which should increase η_{coll} of the electrode. In complementary EIS measurements, low R_w/R_k ratios are noted for devices with the top hybrid layer. Likewise, τ is almost 10 times longer than in the reference devices. As a consequence, η_{coll} is nearly two times higher for devices with the top layer than the reference (see Fig. 5b).

Furthermore, long term stability assays for devices featuring the TiO_2 _Ru_IS top layer and the P25 reference device were realized (Fig. 6 and S6, ESI). Fig. 6 summarizes the changes of the figures-of-merit over time under operation conditions for the multi-layered electrode featuring the TiO_2 _Ru_IS top layer, while Fig. S6, ESI displays a direct comparison of the J-V curves for the multi-layered and P25 reference electrode at different times, respectively. The lifetime of the reference device (P25-based device) is around 100 h, while the application of a top

hybrid layer increases the lifetime to values of 1,000 h (Fig. 6 and S6, ESI). Here, the FF and V_{oc} remain almost constant over the first 1,000 h, while J_{sc} steadily decreases as shown by the changes in the J-V curves.

Quite likely, the device stability goes hand-in-hand with the degradation of the dye over time. After 1,000 h, FF starts to rapidly drop, indicating a second degradation mechanism. To rationalize these findings, the EIS parameters were monitored (Fig. 6). In particular, during the first 500 h, R_w slightly increases, while R_k remains constant, suggesting that the hybrid top layer prevents the degradation of both the electrode and the dye. As such, η_{coll} remains almost constant at around 60%, after an initially sharp decrease. Partial degradation of the dye, as the decrease of τ and J_{sc} suggests, is mainly responsible for this trend. In the range from 500 to 1000 h, both R_w and R_k exponentially increase, hence we conclude that the entire electrode is undergoing degradation. The latter is even more pronounced at around 1,000 h, at which η_{coll} strongly reduces due to prominent electron recombination within the electrolyte (Fig. 6).

In other words, devices featuring TiO_2 _Ru_IS as top electrode display strongly enhanced long term stability compared to the pure P25 reference device.

Fig. 7. Photovoltaic performance and EIS analysis of the It-DSSCs prepared with multilayered P25:NH/ $\text{TiO}_2\text{-Ru_IS}$ electrodes (brown line) in comparison with the devices featuring a single P25:NH layer (blue dotted line). (a) Schematic representation of the electrode setup, (b) figures-of-merit, (c) SEM image of half covered electrode featuring the P25:NH/ $\text{TiO}_2\text{-Ru_IS}$ set up, (d) J-V curves and (e) IPCE's curves of the devices.

Indeed, while the half-life time of P25-based devices is reached after 100 h due to a fast degradation of the dye – and subsequent recombination processes of the electrode with the electrolyte – devices with $\text{TiO}_2\text{-Ru_IS}$ top layers feature strongly enhanced lifetimes of up to 1000 h, thanks to the protective effects of said layer towards dye degradation. The latter points out the advantage of integrating the Ru(II) dye into the structure of titania nanoparticles as a strategy to improve the stability of It-DSSC electrodes.

As such we conclude, that while a $\text{TiO}_2\text{-Ru_IS}$ -based top layer strongly increases device lifetimes, the device efficiency is still lacking. To remedy the latter while keeping the superb lifetimes granted by the protective effects of the $\text{TiO}_2\text{-Ru_IS}$ top layer, the P25 bottom layer will be replaced by the far more efficient P25:NH layers investigated before – *vide supra*.

Low-temperature DSSC based on multi-layered P25:Non-hybrid/ $\text{TiO}_2\text{-Ru_IS}$ electrodes.

To achieve the goal of fabricating highly stable and efficient devices, we manufactured It-DSSCs combining the best electrode architectural features described above. To this end, The bottom layer consisted of P25:NH (in a ratio of 80:20 wt%) to maximize the the J_{sc} , η_{coll} , and, in turn, the overall η of the It-DSSC. Additionally, a pure $\text{TiO}_2\text{-Ru_IS}$ based layer is added on top of the P25:NH bottom layer to increase the lifetime of the device – see Fig. 7a and Experimental Section for more details. This device architecture will be referred as P25:NH/ $\text{TiO}_2\text{-Ru_IS}$ from here on out. This approach should lead to further enhanced efficiencies and stabilities. Indeed, J-V assays show,

that the J_{sc} is enhanced together with the V_{oc} (J_{sc} of $18.06 \text{ mA}/\text{cm}^2$, a V_{oc} of 0.74 V, and a FF of 66 %) leading to a remarkable overall efficiency of 8.75% (Fig. 7).

To elucidate the electronic changes for these devices, EIS assays were realized under dark and illumination at open circuit conditions. The key parameters are depicted in Fig. 7b. As expected, the Nyquist plots are best described as two semicircles (Fig. S7, ESI). A comparison of EIS figures-of-merit prompts two major findings. Firstly, under illumination, R_w is further reduced from 19 to 10Ω for devices featuring a single P25:NH layer and the P25:NH/ $\text{TiO}_2\text{-Ru_IS}$ electrode set up, respectively (Fig. 7b). This is an unequivocal indication for a decreased charge transport resistance (R_w) of the electrodes. Secondly, studies under dark conditions showed that the low-frequency semicircle decreases upon increased amounts of layers, hinting at an increased electron recombination (Fig. S7, ESI). However, when the ratios between R_k and R_w are compared it becomes evident, that the P25:NH/ $\text{TiO}_2\text{-Ru_IS}$ shows a better charge collection efficiency than those of the other devices (Fig. S8, ESI). The same trend applies to τ validating our previous finding, namely, that the electron recombination is indeed lower for the P25:NH/ $\text{TiO}_2\text{-Ru_IS}$ configuration (Fig. 7b).

Finally, long term stability assays for the P25 reference and P25:NH/ $\text{TiO}_2\text{-Ru_IS}$ devices were performed. Severe differences were noted for both devices (see Fig. 8, 9 and S9, ESI). On one hand, the P25 reference device rapidly and linearly loose efficiency (Fig. 9) due to a steady decline in all figures-of-merit, but especially due to a rapid loss in J_{sc} , indicating a swift degradation of the dye starting at day 1.

Fig 8. Changes of the figures-of-merit (left) and the EIS parameters (right) of a P25:NH/TiO₂_Ru_IS device measured over time under operation conditions.

On the other hand, while the P25:NH/TiO₂_Ru_IS device loses efficiency over the measured period of 600 h as well the pattern of decline is radically different (see Fig. 8, 9 and S9, ESI). In particular, the V_{oc} stays constant at the beginning and starts to steeply increase after 300 h. The FF follows the same behavior. The J_{sc} , however, stays constant for the first 300 h and starts to decline afterwards. This further rules the decrease of the device efficiency. As already determined for the long term measurements, the decrease of the J_{sc} is quite likely related to a degradation of the dye over time. This is, however, strongly delayed compared to the P25 reference device pointing out the effectiveness of integrating these novel hybrid dye-TiO₂ nanoparticles into the electrode architecture.

To gain a better insight of the latter findings, the EIS parameters were monitored (see Fig. 8, and Fig. S10 and S11, ESI). In particular, during the first 300 h, R_w and R_k stay constant, suggesting that the hybrid top layer indeed prevents the degradation of both the electrode and the dye. As such, the J_{sc} and η_{coll} remain almost constant at around 18 mA/cm² and 73%, respectively. In the range from 300 to 600 h, both R_w and R_k exponentially increase, from which we conclude the degradation of the entire electrode (Fig. 8 and S11, ESI). The latter is even more pronounced after 400 h, at which time η_{coll} falls below 70 % due to prominent electron recombination with the electrolyte. The latter notion is supported by a sharp decline of the R_k to R_w ratio (Fig. S11, ESI), indicating that not only electron recombination (R_k) is enhanced but also charge transport (R_w) is strongly affected by the deteriorating

electrode. However, only after around 600 h these destructive processes become so pronounced that the half-life time of the device is reached (Fig. 8 and 9).

Fig 9. Relative efficiency decrease of It-DSSCs based on the P25 reference (black dotted line) and P25:NH/TiO₂_Ru_IS electrodes (brown line) over time.

Conclusion

The work at hand provides a new strategy to design It-DSSCs featuring enhanced charge collection efficiencies (η_{coll}), efficiencies (η), and device stabilities by integrating small-sized hybrid (TiO₂_Ru_IS) and non-hybrid (NH) nanoparticles into the electrode architecture. The integration of these dye-TiO₂ hybrid nanoparticles (TiO₂_Ru_IS), obtained by *in-situ* bottom-up

construction of dye-sensitized titania using the Ru(II) N3 dye as building blocks, into the electrodes allow to tackle the two main bottlenecks in It-DSSC, i.e. low stability devices and moderate efficiencies. In detail, devices with optimized electrodes featuring a network that consists of a mixture of P25 and the NH material show a good balance between charge transport and electron recombination. This leads to an increase in J_{sc} and charge collection efficiency (from 46% to 61%), which, in turn, induces an efficiency increase from 2.3% to 5.5% for reference and 80:20 (P25:NH) devices, respectively. Furthermore, the combination of pure P25 and TiO₂_Ru_IS-based layers leads to a 10-fold half-life time increase (from 100 to 1000 h for reference and multilayered devices, respectively) and an increase of η_{coll} to 74% – due to the intrinsic stability characteristics and the high resistance to recombination of TiO₂_Ru_IS. Finally, both approaches are combined – P25:NH bottom layers and TiO₂_Ru_IS top layers – to further enhance the electrode efficiency while keeping the formidable stability. This results in It-DSSCs featuring η_{coll} 's of 72%, lifetimes of 600 h under operation conditions, and extremely high efficiencies of around 8.75%. The latter constitutes the highest efficiency for It-DSSCs in the literature so far.

Experimental

General: Tetrabutyl orthotitanate (TBOT, 97%), absolute ethanol, and titanium-dioxide P25 were purchased from Sigma-Aldrich and used as received without further purification. H₂PtCl₆ was used to prepare the counter-electrodes, as well as 1,2-dimethyl-3-propylimidazolium iodide (Sigma-Aldrich), and 4-tert-butylpyridine were used to prepare the electrolyte. The FTO-glass slides – Pilkington, 3.2 mm, 8 Ω/cm^2 – were purchased from XOP glass.

Preparation of the hybrid TiO₂_Ru_IS: The preparation of the hybrid TiO₂_Ru_IS is based on the one-pot co-condensation of tetrabutyl orthotitanate (TBOT), as titania precursor, and the [Ru(4,4'-H₂dc bpy)₂(SCN)₂] (dye N3), according to our methodology for the *in-situ* integration of different dyes on the structure of the titania nanoparticles. The details are described elsewhere.^{52,53} Briefly, a solution of the synthesized Ru(II) complex in 2 ml of absolute EtOH (0.04 g, 0.06 mmol) was added to 5 g (14.7 mmol) of TBOT. The mixture was stirred during 30 minutes and then dissolved in 35 ml of absolute ethanol, under magnetic stirring. Following, 123.5 g (6.86 mol) of water was added drop-wise, causing the precipitation of the solid. The molar ratio of the synthesis gel was 1TBOT: 4x10⁻³ Ru(II) N3: 41.3 EtOH: 467 H₂O. The mixture was then reacted at room temperature during 24 h under vigorous magnetic stirring, and heated at 80 °C for other 24 hours. The obtained solid product was filtered, washed with water and acetone and dried in an oven at 100 °C for 8 hours. The TiO₂_Ru_IS material was obtained as a pale garnet solid (0.97 g, 80%). The incorporation of the coordination dyes, not only on the surface of the titania, but also into the anatase structure of the hybrid TiO₂_Ru_IS was tested by washing it with a 0.1 M NaOH solution for 2 seconds. The amount of the remaining dye after the basic washing was estimated, based on the maximum absorbance (DRUV) at ca. 500 nm, to be 47 %. Non-hybrid titania nanoparticles (NH) were

prepared following the same procedure without the use of the Ru dye.^{52,53}

Preparation of the TiO₂ pastes: P25-based, NH and TiO₂_Ru_IS pastes were prepared following the method reported by Weerasinghe *et al.*⁶⁰ In detail, 100 mg of the commercial TiO₂-P25 or the NH or TiO₂_Ru_IS was suspended in 400 μL (or 800 μL for diluted pastes) of absolute EtOH under magnetic stirring. Afterwards, 100 μL of a solution with different concentrations of HCl, ranging from 0.5 to 5.5 M, was added to the mixture. The resulting suspensions were stirred at room temperature during 20 hours. The P25:TiO₂_Ru_IS and P25:NH pastes were prepared following the same methodology using the optimal conditions that we noted with the P25-based pastes – i.e., [HCl] = 1 M. In the case of P25:TiO₂_Ru_IS, different amounts of the hybrid TiO₂_Ru_IS – i.e., 0, 10, 20, 30, 50, 70, and 100 wt% – were mixed with the commercial TiO₂-P25 before the suspension of the mixture in absolute ethanol. The P25:NH pastes were also prepared in a similar way, but the P25:NH mass ratio was kept to be 80:20.

Device Fabrication: Fluorine-doped tin oxide (FTO) glass substrates were cleaned with acetone in an ultrasonication bath for 15 min. Afterwards, they were sonicated in a soap solution, pure deionized water, and isopropanol (deconex FPD 120, 1% vol. solution in 150 ml deionized water) each for 15 min. Finally, the substrates were dried under a nitrogen flow and, in order to eliminate any organic residual placed onto the electrode surface, they were further treated in a UV-ozone cleaner model 42-220 (Jelight Company) for 18 min. The cleaned FTO glass substrates were subsequently immersed in an aqueous TiCl₄ solution at 80 °C for 30 min, then washed with water and EtOH, and finally heated at 450 °C during 30 min. The synthesized pastes were subsequently doctor-bladed using a circular Scotch tape template with a diameter of 5 mm and a thickness of 50 μm onto the aforementioned FTO slides. Subsequently, the first layer was dried at 200 °C for 30 min and if mentioned, a top layer of the TiO₂_Ru_IS was applied using first a diluted paste in Ethanol and then the above-mentioned paste. The slides were then cooled to 80 °C. The latter were then immersed for 16 h into a (tert-Butyl alcohol: Acetonitrile 1:1) based 0.5 x 10⁻⁴ M molar N719 ruthenium solution to fully cover the semiconducting surface. For the counter-electrode fabrication, FTO plates with two holes of 1 mm diameter at the edge of the active area were used. Prior to the fabrication of the counter-electrodes, the FTO slides were cleaned following the aforementioned procedure. A thin film was prepared with 26 μL H₂PtCl₆ (0.5 mmol in ethanol, ~38 wt% Pt content) that were directly spread over the FTO plates and dried in air prior baking at 400 °C for 20 min. To finalize the device, both electrodes were sealed together with a transparent film of 25 μm Surlyn (DuPont Ltd., UK) cut as a frame around the nanocrystalline film. A solution of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide 99 %, 0.05 M iodine double sublimed, Lithium iodide 0.1 M, and 0.5 M 4-tert-butylpyridine 96 % in a solvent mixture of acetonitrile and valeronitrile (85:15 v/v) was employed as electrolyte. The electrolyte was introduced through the aforementioned holes and the final cell was sealed immediately afterwards using another piece of Surlyn, and a piece of microscope slide.

Characterization of the electrodes: Thermogravimetric analyses (TGA) were carried out in a Mettler Toledo TG-ATD

(TGA/SDTA851e/sf/110). The measurements were carried out under nitrogen/oxygen atmosphere (4:1) from room temperature to 900 °C, with a heating rate of 10 °C/min. The morphology of the P25:TiO₂-Ru-IS electrodes before being immersed in the N719 ruthenium solution was analyzed by Scanning Electron Microscopy (SEM) using a Zeiss Gemini 55 Ultra electron microscope under vacuum (10⁻⁹ mbar). Relative changes in roughness were calculated via profilometry (DektakXT from Bruker) by using as a reference the pure P25 electrode, as well as via desorption studies upon increasing the hybrid amount in the electrode. The roughness average was calculated by accumulating several profilometry scans of the whole surface and using an analytical Gaussian method already implemented in the software. UV-Vis spectroscopy was used in order to determine the amount of dye molecules attached to the surface of TiO₂ layers and the roughness average via desorption experiments using a UV-VIS-NIR Scanning Spectrometer from Shimadzu. In detail, after soaking the slides into dye solution for 16 h, they were immersed in 3 mL of 1 M NaOH solution until all the dye molecules were desorbed from the layers. Since the concentration of dye solution is directly proportional to the absorbance of light, the amount of dye molecules adsorbed was calculated from the absorbance peak of UV-vis spectrum of solution at 503 nm. Here, R is defined as the total active surface area per unit substrate area as given by equation 1,⁶¹

$$R = D_{ad} \times N_A \times D_A \quad (1)$$

where D_{ad} is the quantity of the dye adsorption per unit area (mol/nm²), N_A for Avogadro's number, and D_A for the area per dye molecule, which is 1.6 nm²/dye molecule for N719.⁶⁰ D_{ad} was obtained by absorption spectroscopic measurements as above explained.

Photovoltaic evaluation of It-DSSCs: Photocurrent measurements were carried out under AM 1.5 conditions using a custom-made solar simulator, including a 350-1000 Watt adjustable Xe lamp source (LOT) combined with an appropriate AM 1.5 filter. Current voltage measurements were performed by using a potentiostat/galvanostat (PGSTAT30, Autolab) in the range from -0.8 to 0.2 V. All measurements were performed with a black mask after calibration of the aforementioned apparatus with a silicon solar cell reference SRC-1000-TC-K-KG5-N pursued from VLSI standards at room temperature. Incident photon-to-current efficiency (IPCE) was measured by using a Newport apparatus model 70104.

Electrochemical Impedance measurements: Electrochemical impedance spectroscopic assays (EIS) were carried out with a potentiostat/galvanostat (PGSTAT30, Autolab) equipped with a frequency response analyzer module (FRA). Measurements were performed at the respective open-circuit voltage of the different devices in the dark and under illumination (AM 1.5 filter, 1000 W/cm²). The AC signal amplitude was set to 10 mV, modulated in a frequency range from 0.1 to 100 KHz. The Nova 1.11 software was used to obtain the parameters from the equivalent circuit. With this data at hand, the charge collection efficiency (η_{coll}) and electron lifetime (τ) were calculated by means of equations 2 and 3, respectively

$$\eta_{coll} = 1 - (R_w/R_k) \quad (2)$$

$$\tau = 1/(2 \times \pi \times f_{max}) \quad (3)$$

where R_w , R_k , and f_{max} , are the electron transport resistance, the charge-transfer resistance to recombination of electrons and the maximum frequency taken from the Bode phase plot, respectively.

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