Light-induced charge transfer at the CH$_3$NH$_3$PbI$_3$/$\text{TiO}_2$ interface—a low-temperature photo-electron paramagnetic resonance assay

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Abstract

The performance of organic–inorganic metal halide perovskite-based (MHPs) photovoltaic devices critically depends on the design and material properties of the interface between the light-harvesting MHP layer and the electron transport layer (ETL). Therefore, the detailed insight into the transfer mechanisms of photogenerated carriers at the ETL/MHP interface is of utmost importance. Owing to its high charge mobilities and well-matched band structure with MHPs, titanium dioxide (TiO$_2$) has emerged as the most widely used ETL material in MHPs-based photovoltaic devices. Here, we report a contactless method to directly track the photo-carriers at the ETL/MHP interface using the technique of low-temperature electron paramagnetic resonance (EPR) in combination with in situ illuminations (Photo–EPR). Specifically, we focus on a model nanohybrid material consisting of TiO$_2$-based nanowires (TiO$_2$NWs) dispersed in the polycrystalline methylammonium lead triiodide (MAPbI$_3$) matrix. Our approach is based on observation of the light-induced decrease in intensity of the EPR signal of paramagnetic Ti$^{3+}$ ($S = 1/2$) in non-stoichiometric TiO$_2$NWs. We associate the diminishment of the EPR signal with the photo-excited electrons that cross the ETL/MHP interface and contribute to the conversion of Ti$^{3+}$ states to EPR-silent Ti$^{2+}$ states. Overall, we infer that the technique of low-temperature Photo–EPR is an effective strategy to study the transfer mechanisms of photogenerated carriers at the ETL/MHP interface in MAPbI$_3$-based photovoltaic and photoelectronic systems.

1. Introduction

Recently, organic–inorganic metal halide perovskites (MHPs) have attracted considerable attention in various domains of optoelectronics, including light emission, sensing and photovoltaics (see [1] and references therein), due to their excellent photophysical properties, such as high light absorption coefficient, technologically-tunable bandgap, absence of deep trap states within the bandgap, high charge mobility and long diffusion lengths as well as excellent photoluminescence quantum yield.

Such a variety of attractive properties of MHPs accompanied also by their low-cost solution processability, sparked the interest to use these materials in a large number of optoelectronic systems [2, 3]. Currently, the most prominent implementations are solar cells [4], lasers [5] and light-emitting diodes [6].

Recent advances in technologies of preparation and processing of MHPs largely enhanced the conversion of solar energy into an electrical current. Consequently, over a period of only a few years, MHPs-based solar cells have seen a remarkable rise in power conversion efficiencies (PCEs) from the initial 3.8% [7] and 9.7% [8] to the...
currently certified record of 25.2% \[9\]. Specifically, due to better engineering of the electron and hole transport layers (hereinafter ETLs and HTLs), the charge extraction from MHPs has been significantly improved.

In parallel to applications in photovoltaics, a number of studies have also investigated a variety of MHPs-based detectors and sensors, including x-ray detecting devices \[10\], near-ultraviolet to near-infrared (330–800 nm) light detectors \[5, 11–13\], tactile sensors \[14\], as well as gas \[15\] and even high-energy particle detectors \[16\].

In general, the above-mentioned devices were designed as planar structures. Therefore, for serving specific purposes, their architectures required a stack of various kinds of functional thin layers. In consequence, besides MHP-based light-harvesting layers, the other most investigated elements of the stacked planar architectures were the ETLs and HTLs, as well as the device terminal electrodes \[11, 17–21\].

Despite recent progress in the technology of functional layers and device configurations, TiO\(_2\) is still most commonly used for designing ETLs in MHP-based devices. TiO\(_2\) offers a number of important advantages, including chemical stability, nontoxicity, high charge mobilities, well-matched band structure with MHPs, low-cost and simple fabrication procedures \[22\]. It has been shown that the performance of TiO\(_2\)-based ETLs could be largely improved through bandgap-engineering by doping with transition metal \[23\] or nonmetal elements \[24, 25\], surface functionalization \[26\], photosensitization \[27\] and heterojunction preparation \[28\]. In fact, the recent surge of interest in perovskite-based devices opened a new research area oriented towards optimization of both the physicochemical properties of TiO\(_2\) itself and the morphology of its interface with MHPs.

The archetypal halide perovskite and also the first successfully employed MHP in solar cells, methylammonium lead triiodide, CH\(_3\)NH\(_3\)PbI\(_3\) (hereinafter MAPbI\(_3\)), is continuing to be used as a model material to study the transfer mechanisms of light-generated carriers in various types of bilayer MHP/ETL or MHP/HTL systems \[29–31\].

There have been several reports on the transfer mechanisms of photogenerated carriers at the interfaces between MHPs and the electron-transporting materials, such as TiO\(_2\), or hole-transporting materials, such as Spiro-OMeTAD or PCBM \[32–34\]. Time-resolved techniques, such as transient absorption (TA), photoluminescence (TRPL), and terahertz absorption (TRTS) spectroscopies, or time-resolved microwave photoconductivity (TRMC) were the most popular approaches used in these investigations \[35\].

Despite intensive research, the direct observation of the transfer of photogenerated carriers at the MHP/ETL interface still remains a challenge. This complicates gaining insight into the role of surface and bulk defects at the MHP/ETL interface and to better understand their influence on the device performance.

Therefore, in this work, we aim to advance the understanding of the charge transfer mechanisms of light-generated carriers in bilayer MHP/ETL systems. In particular, we show that the technique of electron paramagnetic resonance (EPR) in combination with \textit{in situ} illuminations (Photo-EPR) can be used to directly monitor the charge transfer from MAPbI\(_3\) to TiO\(_2\), as well as to determine the exact number of trapped electrons by the TiO\(_2\) surface defects.

Specifically, we report a low-temperature Photo-EPR study performed on a model nanohybrid system consisting of TiO\(_2\) nanowires (TiO\(_2\)NWs) dispersed in a polycrystalline MAPbI\(_3\) matrix. Our approach is based on observation of the light-induced decrease in intensity of the EPR signal of paramagnetic species of trivalent titanium (Ti\(^{3+}\), \(S = 1/2\)) in TiO\(_2\)NWs. Prior to low-temperature EPR measurements, in order to enhance the concentration of Ti\(^{3+}\) species, TiO\(_2\)NWs were thermally-reduced in hydrogen (H\(_2\)) atmosphere. The thermal reduction process resulted not only in the formation of a large concentration of Ti\(^{3+}\) centers but was also accompanied by a marked colour change of the TiO\(_2\)NWs: from white to blue. Therefore, hereinafter, non-reduced (oxidized) TiO\(_2\)NWs and thermally-reduced TiO\(_2\)NWs, are referred to as white-TiO\(_2\)NWs and blue-TiO\(_2\)NWs, respectively.

The observed diminishment of the EPR signal upon illumination with the green laser light (\(\lambda_{\text{exc}} = 532\) nm) is associated with the photo-excited electrons that cross the MHP/ETL interface between the grains of polycrystalline MAPbI\(_3\) and dispersed blue-TiO\(_2\)NWs, thus leading to the conversion of paramagnetic states of Ti\(^{3+}\) to the EPR-silent Ti\(^{4+}\) states. We also demonstrate that a combination of the low-temperature Photo-EPR with light modulation and lock-in detection allows one to gain additional insight into the temporal evolution of the photo-excited carriers at the MHP/ETL interface. With both techniques we successfully identified that ~20% of the surface species in blue-TiO\(_2\)NWs trapped photogenerated electrons.

Furthermore, to prove the validity of our Photo-EPR-based approach, we also set up a complementary proof-of-principle study centered on a visible light photodetector, which was designed around a junction formed between a single crystal of MAPbI\(_3\) and compacted TiO\(_2\) powder. Specifically, to make it function as a light detector, a single MAPbI\(_3\) crystal was brought into electrical contact with a pellet made from TiO\(_2\)NWs. We found that the diode-like performance of this simple photodetector was markedly dependent on the type of TiO\(_2\)NWs used to form the pellet. In particular, both the forward photo-current and the rectification ratio were largely improved while employing the pellet made of blue-TiO\(_2\)NWs as compared to the pellet formed from white-TiO\(_2\)NWs. These two factors, resulting from an improved electrical conductivity and concomitant
enhanced charge extraction from MAPbI$_3$, contributed to a higher light-sensitivity of the photodetector consisting of a single crystal of MAPbI$_3$ and the pellet made of blue-TiO$_2$NWs.

2. Experimental methods

2.1. Preparation of a stoichiometric solution of MAPbI$_3$
Firstly, prior to preparing the saturated DMF solutions of MAPbI$_3$, it was necessary to prepare stoichiometric single crystals. Accordingly, MAPbI$_3$ single crystals were made by precipitation from an aqueous solution of concentrated hydroiodic acid (37 wt% in H$_2$O), containing stoichiometric amounts of lead(II) acetate trihydrate (Pb(ac)$_2$·3H$_2$O) and methylamine (CH$_3$NH$_2$, 40 wt% in H$_2$O). MAPbI$_3$ crystals were grown and recrystallized in the saturated hydroiodic acid solution applying temperature gradient in the vessel. The crystals were dissolved at the higher temperature side of the vessel and recrystallized at the lower temperature side of the vessel [10]. Subsequently, the obtained MAPbI$_3$ single crystals were harvested, dried at 120 °C and dissolved in DMF, leading to a 30 wt% DMF stock solution.

2.2. Opto-electronic characterization of the interface of MAPbI$_3$ and TiO$_2$NWs
The junctions in between MAPbI$_3$ and different versions of TiO$_2$NWs have been characterized by means of two-point resistance measurements at ambient conditions. One of the tungsten probe electrode needles has been placed on top of the MAPbI$_3$ crystal, pressing it against a white or blue TiO$_2$ pellet, while the second needle has been placed on the TiO$_2$ pellet, close to the crystal. A Keithley 2400 source meter allows for measurements of the current with <0.1 nA resolution while tuning the applied bias voltage. All measurements were made under white light illumination using a light intensity of 1.02 mW cm$^{-2}$.

For all opto-electronic characterization experiments, we used the same MAPbI$_3$ crystal and identical electrode configurations.

2.3. Preparation of blue-TiO$_2$NWs samples
Protonated titanate (H$_2$TiO$_3$) nanowires were prepared by a two-step hydrothermal process. The details about the typical synthesis procedure are given elsewhere [36]. As described in [37], the white powder of layered protonated titanate nanowires (TiO$_2$NWs) is heat-treated in H$_2$ flow at 600 °C for 1h. The cyan coloured hydrogenated titanium oxide nanowires (blue-TiO$_2$NWs) product was cooled fast to room temperature. Heat treatment of blue-TiO$_2$NWs in the air at 450 °C or 550 °C for 30 min resulted in white TiO$_2$NWs. The colour change from cyan to white is instantaneous upon heat treatment.

2.4. Synthesis of reduced TiO$_2$ single crystals
High-quality single crystals of blue TiO$_2$ anatase were produced by a chemical transport method from anatase powder using ammonium chloride (NH$_4$Cl) as a transport agent, following a modified procedure based on the one described in [38]. In brief, ~3.0 g of high-purity sintered powder of anatase (99.6% pure, 3–6 mm sized grains, from Merck) were sealed together with ~0.4 g of NH$_4$Cl (Merck) in a ~20 cm long, 2.0 cm in diameter, quartz ampule. Before sealing, the reagents were thoroughly dried out and evacuated at pressure <4 × 10$^{-6}$ mbar during one night.

Subsequently, the sealed ampule was placed in a horizontal tubular two-zone furnace and heated slowly to 750 °C and 600 °C, at the source and the deposition zones, respectively. After ~5–8 weeks, millimeter-sized crystals (~1.5 × 1.5 × 1.5 mm$^3$) with a bi-pyramidal shape were collected.

The microcrystalline powder (0.01–0.5 mm average grain sizes) of blue TiO$_2$ anatase was obtained by careful grinding of two-three small (ca. 2–3 mm$^3$) single crystals of blue TiO$_2$ anatase in an agate mortar. The ground material conserved the same deep-blue colour as the starting monocrystalline blue TiO$_2$ anatase.

2.5. Preparation of MAPbI$_3$/TiO$_2$ nanohybrid material
To prepare the nanohybrid structures, we mixed 20 mg of the TiO$_2$ samples (ground TiO$_2$ crystallites, white- and blue-TiO$_2$NWs powder, or Tayca Corp. AMT-600 anatase powder) with 100 μl of MAPbI$_3$ precursor solution. The nanohybrid of MAPbI$_3$ and TiO$_2$ samples were coated on the surface of d = 2 mm diameter quartz rods serving as light guides.

Due to a substantial difference in refractive indices between MAPbI$_3$ (n ≈ 2.8) [39], TiO$_2$ (n ≈ 2.6) [40] and quartz (n ≈ 1.46) [41] our approach made it possible to efficiently extract light from the quartz light guide to the whole surface of the deposited material. Figure 3(b) provides exemplary proof of very efficient extraction of the green laser light (λ$_{exc} = 532$ nm) from the quartz-made sample holder to a thin deposit of white-TiO$_2$NWs.

For reference measurements, TiO$_2$ samples (ground TiO$_2$ crystallites, white- and blue-TiO$_2$NWs powder, or Tayca Corp. AMT-600 anatase powder) were mixed with 1 mg of polyethylene oxide (PEO, 100 000 MW) and
supplemented with 90% of ethanol and 10% distilled water to make a suspension. The mixture was then used to coat the \( d = 2 \text{ mm} \) quartz rods implemented as light guides for illumination experiments.

Here, we do not implement MAPbI\(_3\) as a reference sample, as our previous investigations showed that MAPbI\(_3\) remained EPR-silent both in the dark and under illumination \([42]\).

### 2.6. EPR experiments

Low-temperature continuous-wave ESR measurements were carried out with a Bruker ESR spectrometer E500 EleXsys Series (Bruker Biospin GmbH) equipped with a Gunn diode-based microwave bridge (model SuperX), a Bruker ER 4122 SHQE cavity and an Oxford Instruments Helium-gas continuous flow cryostat (ESR900).

A conventional field-modulation technique combined with lock-in detection has been used for measurements in the dark and under continuous illumination, which resulted in the first derivative of the EPR absorption spectra. For the experiment conducted under synchronously modulated illumination the magnetic field modulation has been substituted by modulation of light, once again combined with lock-in detection. The latter scheme yielded directly the EPR absorption signal instead of its first derivative as for conventional measurements performed either in the dark or under continuous illumination. Such an approach, while taking advantage of the lock-in detection technique, has been chosen to highlight the light-induced changes. The working principles of the two methods are shown in more detail in figure S6.

### 2.7. Light sources for illumination of the nanohybrid samples

Illumination for field-modulated EPR measurements (i.e. for light-on spectra) was provided by different light sources: (i) a green, \( \lambda = 532 \text{ nm} \) laser at an illumination power of 20 mW (Laser Quantum Ltd.); (ii) by a red, \( \lambda = 660 \text{ nm} \), 50 mW AlGaInP laser diode (ADL-6650TL); (iii) by a halogen lamp; or by (iv) an ultraviolet lamp with an illumination intensity of 20 or 40 mW.

The illumination for light-modulated EPR measurements was provided by a red, \( \lambda = 660 \text{ nm} \), 50 mW AlGaInP laser diode (ADL-6650TL). The light modulation was performed using an Agilent 33250A 80 MHz Function/Arbitrary Waveform Generator.

Calibration of the light intensity was performed by connecting a calibrated photodiode to a Stanford Research Systems model SR830 DSP lock-in.

### 3. Results and discussion

#### 3.1. MAPbI\(_3\)/blue-TiO\(_2\)NWs-based visible light photodetector

To prove the concept of enhanced light-induced charge transfer at the MAPbI\(_3\)/blue-TiO\(_2\)NWs interface, we designed a visible light photodetector. To this end, a single crystal of MAPbI\(_3\) was brought into electrical contact by dry-pressing (described in detail in \([43]\)) with a pellet made of either blue-TiO\(_2\)NWs or white-TiO\(_2\)NWs.

The photographic images of the starting material for preparation of TiO\(_2\)NWs pellets, i.e. protonated layered titanate H\(_2\)Ti\(_3\)O\(_7\) nanowires (TiO\(_2\)NWs), as well as thermally-reduced (blue-TiO\(_2\)NWs) and thermally re-oxidized TiO\(_2\)NWs (white-TiO\(_2\)NWs), are shown in figure 1(a). As can be seen, thermal reduction in hydrogen atmosphere at 600 °C transforms the original white-coloured powder of TiO\(_2\)NWs into a blue-coloured powder (blue-TiO\(_2\)NWs). The subsequent calcination in air at either 450 °C or 550 °C converts blue-TiO\(_2\)NWs back to the white-coloured material (white-TiO\(_2\)NWs). Hereinafter, the two versions of the latter re-oxidized material are referred to as white-TiO\(_2\)NWs(450 °C) and white-TiO\(_2\)NWs(550 °C), respectively.

We have shown previously that blue-TiO\(_2\)NWs and both white-TiO\(_2\)NWs(450 °C) and white-TiO\(_2\)NWs(550 °C) reveal the same anatase-like crystal structure \([37]\). The major difference between the reduced (blue-TiO\(_2\)NWs) and re-oxidized (white-TiO\(_2\)NWs) versions of this material is in their content of paramagnetic Ti\(^{3+}\) surface states, which is at least three orders of magnitude higher for blue-TiO\(_2\)NWs, thus reaching ~1% of the total concentration of the surface titanium ions \([37]\).

The schematic band structure diagram at the MAPbI\(_3\)/blue-TiO\(_2\)NWs interface is shown in figure 1(c). As indicated, the population of Ti\(^{3+}\) surface states provides shallow donor levels located from 0.3 to 0.7 eV below the conduction band (CB) minimum of TiO\(_2\) \([44, 45]\). It has been generally accepted that these Ti\(^{3+}\) species are occupied states and usually act as donors, thus largely contributing to the improved electrical conductivity of blue-TiO\(_2\)NWs. The electrons in these sites can be excited into the CB either by a thermal or photoexcitation process to form the unoccupied states \([46, 47]\). Correspondingly, the herein observed marked colour change can also be ascribed to enhanced absorption of the visible and near-infrared light by Ti\(^{3+}\) surface states in blue-TiO\(_2\)NWs \([48]\).

The \( I-V \) characteristics acquired under visible light illumination for the described simple photodetector are shown in figure 1(b). The scheme of the MAPbI\(_3\)/TiO\(_2\) photo-junction is shown in the inset to figure 1(b). All the \( I-V \) characteristics exhibited a diode-like behaviour for three different materials used to form the TiO\(_2\)NWs pellets, i.e. blue-TiO\(_2\)NWs, white-TiO\(_2\)NWs(450 °C) and white-TiO\(_2\)NWs(550 °C). However, both the forward
photo-current and the rectification ratio were markedly superior for the device consisting of a single MAPbI3 crystal brought into electrical contact with the pellet made of blue-TiO2NWs. The I–V characteristics collected for the devices employing the pellets made of either white-TiO2NWs (450 °C) or white-TiO2NWs (550 °C), were practically identical. This observation suggests that the charge transport properties of white-TiO2NWs do not differ significantly for the material calcinated at either 450 °C or 550 °C. The hysteretic character of the recorded I–V curves can be ascribed to the presence of mobile ions and their slow migration through the perovskite material, as reported earlier [49, 50].

In figure 1 (d), we show the corresponding photo-current transients, whereby illumination with the visible light was consecutively turned on and off. The strongest responses to the dark-light illumination conditions were observed for the photo-junction consisting of a single MAPbI3 crystal brought into electrical contact with the pellet made of blue-TiO2NWs. The I–V characteristics collected for the devices employing the pellets made of either white-TiO2NWs (450 °C) or white-TiO2NWs (550 °C), were practically identical. This observation suggests that the charge transport properties of white-TiO2NWs do not differ significantly for the material calcinated at either 450 °C or 550 °C. The hysteretic character of the recorded I–V curves can be ascribed to the presence of mobile ions and their slow migration through the perovskite material, as reported earlier [49, 50].

In figure 1 (d), we show the corresponding photo-current transients, whereby illumination with the visible light was consecutively turned on and off. The strongest responses to the dark-light illumination conditions were observed for the photo-junction consisting of a single MAPbI3 crystal and the pellet made of blue-TiO2NWs. Notwithstanding, the rise times are similar for all the photo-junctions, being of ~0.1 s. In contrast, the fall times are different, being of ~1.0 s and ~1.8 s, for photo-junctions employing blue-TiO2NWs and white-TiO2NWs, respectively. Shorter fall times observed for the photo-junction employing blue-TiO2NWs can be explained by a larger concentration of shallow donor traps in the thermally-reduced TiO2NWs, which leads to faster recombination of the injected charges.

3.2. Quantification of the charge transfer at the MAPbI3/blue-TiO2NWs interface: a photo-EPR study
To quantify the effect of the charge transfer at the interface between MAPbI3 and TiO2 and to gain insight into the underlying mechanisms, we performed low-temperature Photo-EPR measurements on a model nanohybrid system consisting of blue-TiO2NWs dispersed in a polycrystalline MAPbI3 matrix. In this approach, thermally-reduced TiO2NWs (blue-TiO2NWs), containing a large concentration of paramagnetic species of trivalent titanium (Ti3+, S = 1/2), was used as a model for the ETL. Moreover, the dispersion of blue-TiO2NWs in polycrystalline MAPbI3 ensured a large distributed surface of the MAPbI3/blue-TiO2NWs interface.
The morphological characterization of blue-TiO$_2$NWs and the MAPbI$_3$/blue-TiO$_2$NWs nanohybrid material is presented in figure 2. Specifically, figure 2(a) shows the SEM image of the thin deposit consisting solely of blue-TiO$_2$NWs. Blue-TiO$_2$NWs form a highly interlaced pattern in a thin-film deposit, while an individual blue-TiO$_2$NW, has a large length-to-width aspect ratio, with $\sim 5$–10 $\mu$m in length and $\sim 10$ nm in width.

Subsequently, the morphological features of the MAPbI$_3$/blue-TiO$_2$NWs nanohybrid material are shown in figures 2(b)–(d). In particular, the presence of blue-TiO$_2$NWs can be concluded from the SEM image of the nanohybrid material (figure 2(b)). Although, due to a big difference in sizes, this SEM image is dominated by markedly bigger MAPbI$_3$ microwires, numerous agglomerates of blue-TiO$_2$NWs can also be seen. They form randomly distributed protuberances on the relatively regular pattern of MAPbI$_3$ microwires. At the same time SEM element analysis, seen in figure S1 was performed for three elements seen as an overlap over an SEM image in figure S1(a) and found as an element distribution histogram in figure S1(b). Separate element distribution maps are also presented for iodine (figure S1(c)), lead (figure S1(d)) and titanium (figure S1(e)), the first two corresponding to the distributions of MAPbI$_3$ and the latter to the distribution of blue-TiO$_2$NWs in a MAPbI$_3$/blue-TiO$_2$NWs nanohybrid deposit. These element maps clearly show a homogeneous distribution of the three above-mentioned elements providing further evidence of homogeneous spread of blue-TiO$_2$NWs on MAPbI$_3$ microwires.

The inclusions of blue-TiO$_2$NWs are also visible in the optical microscopy and fluorescence images (figures 2(c) and (d)). In particular, in the fluorescence image acquired under $\lambda_{exc} = 546$ nm excitation, agglomerates of blue-TiO$_2$NWs can be seen as darker spots that partially overlap the luminescent microwires of MAPbI$_3$ (figure 2(d)). The corresponding relatively narrow luminescence spectrum, peaking at 772 nm (FWHM = 48 nm), is typical for thin deposits of polycrystalline MAPbI$_3$.

It is noteworthy to mention that thin-film deposits of MAPbI$_3$ coated by single-step solution casting from neat DMF solutions very often appear to show microwire- or fibre-like surface morphology [51]. We also have previously reported similar microwire-like morphology and practically identical luminescence characteristics for single-step solution cast deposits of MAPbI$_3$ on various types of both curved and flat substrates (microwires with sizes of $\sim 8$ $\mu$m in diameter and up to $\sim 150$ $\mu$m in length were observed for small substrates’ curvatures or
The experimental setup used for low-temperature Photo-EPR measurements oriented towards the detection and quantization of photo-generated charges at the MAPbI₃/blue-TiO₂ NWs interface is depicted in figure 3. As schematically shown, a 2 mm diameter rod made of clear fused quartz was implemented to position the sample and deliver light into the EPR cylindrical cavity (TE₀₁₁) resonator (figure 3(a)). The deposits of all the studied materials, including the MAPbI₃/blue-TiO₂ NWs nanohybrid, were directly coated on the outer surface of the quartz rod by dip-coating. Only the bottom part of the quartz rod, which protruded into the EPR resonator, was coated. Thin-film deposits of the commercially available anatase (AMT600, Tayca Corp.), as well as of white-TiO₂ NWs and blue-TiO₂ NWs, suspensions in ethanol incorporating also small amounts of polyethylene oxide (PEO) and water (10%), while, as discussed above, the MAPbI₃/blue-TiO₂ NWs nanohybrid was coated from the stoichiometric solution of MAPbI₃ in DMF, which contained suspended blue-TiO₂ NWs (for more details see section 2 and supplementary material).

The most important findings of this work stemming from the low-temperature Photo-EPR study of photo-generated charges at the model MHP/ETL interface are summarized in figure 4. The comparative EPR evaluation of three TiO₂-based materials having the potential for applications in a model MAPbI₃/TiO₂ system is shown in figure 4(a). Specifically, the stacked plot in this figure compiles normalized EPR spectra acquired at 20 K for the commercially available anatase (black trace), white-TiO₂ NWs (red trace) and blue-TiO₂ NWs (blue trace).

Although all three spectra reveal the presence of paramagnetic species, it can be concluded that blue-TiO₂ NWs provide the strongest EPR-detectable feature (blue trace). In particular, as discussed in details in [53], the strong EPR signal observed for blue-TiO₂ NWs corresponds to a powder EPR spectrum of the surface-located Ti³⁺ paramagnetic centers. We demonstrate our general approach to study the interface using the blue-TiO₂ NWs due to the large Ti³⁺ surface defect concentration and the corresponding large EPR signal intensity. For distorted (tetragonally-elongated) octahedral sites this signal can be fitted with a uniaxial powder distribution having two g-factor components: parallel ($g_|| = 1.94$) and perpendicular ($g_\perp = 1.97$) ([53] and references therein). The temperature dependence of the EPR signal intensity confirmed the Curie-type behaviour for these Ti³⁺-related paramagnetic centers in blue-TiO₂ NWs (see supplementary material, figure S4.). The overall concentration of paramagnetic Ti³⁺ centers in blue-TiO₂ NWs, estimated in our previous publication, was found to be of ~0.4% of all the surface Ti cations [37].
The much weaker EPR spectrum recorded for white-TiO₂NWs (red trace) can be interpreted as originating mostly from paramagnetic oxygen vacancies, $V'_O$ (the narrow peak at $g \approx 2.003$) [54], and a low concentration of bulk-located Ti³⁺ centers (at $g$-factor values of $\approx 1.99$ and $\approx 1.96$).

Interestingly, the traces of Ti³⁺ paramagnetic centers can also be observed for the untreated commercial anatase (weak signals at $g$-factor values of $\approx 1.97$ and $\approx 1.94$). However, the overall EPR spectrum of this material (black trace) is clearly dominated by a broadened signal with $g$-factor values of $\approx 2.029$, $\approx 2.011$ and $\approx 2.003$, which can be ascribed to the adsorbed reduced oxygen molecules and structural oxygen species, i.e. superoxide and oxygen ($O_2^-$/$O^-$) radicals [55, 56].

Figure 4(b) reports the EPR spectra acquired for the deposit of blue-TiO₂NWs under illumination with the green laser light ($\lambda_{exc} = 532 \text{ nm}, P = 20.0 \text{ mW}$) and dark conditions. In the present study, this sample, consisting solely of the thermally-reduced TiO₂NWs, served as a reference for the MAPbI₃/blue-TiO₂NWs nanohybrid material. It can be seen that the EPR spectra recorded for blue-TiO₂NWs in the dark and under illumination perfectly overlap each other. As discussed before, both ESR spectra correspond to Ti³⁺ paramagnetic centers with their characteristic powder distribution with $g$-factor values of $g_1 = 1.94$ and $g_\perp = 1.97$.

In contrast, as shown in figure 4(c), the EPR signal of Ti³⁺ centers in the thin-film deposit of the MAPbI₃/blue-TiO₂NWs nanohybrid material markedly diminishes under identical illumination conditions. Thus, the observed reduction of the EPR signal upon illumination can be associated with the transfer of photo-excited electrons from MAPbI₃ to blue-TiO₂NWs. In particular, the light-excited non-equilibrium electrons in MAPbI₃ cross the interface at grain boundaries between MAPbI₃ polycrystals and dispersed blue-TiO₂NWs, thus leading to conversion of Ti³⁺ EPR-active centers ($d^1$, $S = 1/2$) to EPR-silent Ti²⁺ states ($d^2$, $S = 0$). The light-induced drop in the EPR signal intensity for the herein studied MAPbI₃/blue-TiO₂NWs nanohybrid material was ∼20% at 20 K.
Temperature evolutions of the EPR-detected charge transfer for the deposit of MAPbI$_3$/blue-TiO$_2$NWs nanohybrid material and the reference sample, i.e. the deposit consisting solely of blue-TiO$_2$NWs, are shown in figure 4(d). It can be seen that the ratio of the EPR signal intensities acquired for the deposit of MAPbI$_3$/blue-TiO$_2$NWs nanohybrid material under illumination and dark conditions is markedly lower than unity, adapting values from $\sim$0.8 to $\sim$0.9 in the temperature range of 5–80 K (blue dots). In contrast, the corresponding EPR signal intensity ratio for the reference sample remains close to unity and is practically independent of temperature (red dots). It is worth mentioning that with increasing temperatures the line-width of the Ti$^{3+}$-related EPR signal rapidly broadens up, thus rendering difficult the EPR measurements at temperatures higher than 100 K (for details see supplementary material, figure S4).

The observed light-induced changes were fully reversible and the EPR signal recovered its initial amplitude under dark conditions. This phenomenon was observed for the MAPbI$_3$/blue-TiO$_2$NWs nanohybrid deposit under illumination at different wavelengths. However, the most prominent effect, corresponding to ca. 20% drop of the ESR signal intensity, occurred under illumination with the green laser light ($\lambda_{\text{exc}} = 532$ nm).

As can be deduced from the band structure diagram of the MAPbI$_3$/blue-TiO$_2$NWs interface (figure 1(c)), the photon energy at this wavelength (2.33 eV) is lower than the energy of intraband Ti$^{3+}$ states, which are located ca. 0.5–0.7 eV below the edge of the CB of TiO$_2$. Therefore, the light-induced excitation under illumination at 532 nm wavelength takes place within the narrow-band semiconductor, MAPbI$_3$, whereas blue-TiO$_2$NWs serve as a unidirectional electron sink with an enhanced electron trapping efficiency due to the presence of Ti$^{3+}$ species.

Since our experimental setup was not optimized for performing time-resolved Photo-EPR experiments, we also performed an additional experiment in which the standard modulation of the magnetic field was replaced by modulation of the light source. This approach made it possible to excite the investigated sample with intensity-modulated light using modulation frequencies in the range 1–50 kHz (for details see supplementary material). Based on this procedure, we found that both the light-induced ESR signal decay and its recovery in the dark were faster than the experimental frequency limit of the light modulation (~50 kHz), thus shorter than 20 $\mu$s.

3.3. Conclusions

Taken together, we report a contactless method to directly track photo-carriers at the ETL/MHP interface in a model system consisting of TiO$_2$-based nanowires (TiO$_2$NWs) dispersed in the polycrystalline MAPbI$_3$ matrix. Specifically, thermally-reduced TiO$_2$NWs (blue-TiO$_2$NWs), containing a large concentration of Ti$^{3+}$ paramagnetic centers, were used as the representative material for the ETL. The dispersion of blue-TiO$_2$NWs in polycrystalline MAPbI$_3$ ensured a large distributed surface of the MAPbI$_3$/blue-TiO$_2$NWs interface.

The technique of low-temperature EPR in combination with in situ illuminations (Photo-EPR) was implemented to monitor the light-induced changes in concentration of Ti$^{3+}$ paramagnetic centers in blue-TiO$_2$NWs. In particular, we find that under illumination with the green laser light ($\lambda_{\text{exc}} = 532$ nm) the concentration of Ti$^{3+}$ species in blue-TiO$_2$NWs drops by ca. 20%. This process can be understood in terms of the transfer of light-excited non-equilibrium electrons from MAPbI$_3$ to blue-TiO$_2$NWs, which in turn leads to conversion of EPR-active Ti$^{2+}$ centers ($d^1$, $S = 1/2$) to EPR-silent Ti$^{+}$ states ($d^2$, $S = 0$).

It is also worth noting that the above-mentioned results, stemming from low-temperature Photo-EPR measurements, corroborate the findings for a model ETL/MHP junction, which was formed by bringing into contact the compacted powder of TiO$_2$NWs with a single crystal of MAPbI$_3$. In particular, based on the I–V characteristics of such a simple light detector, we show that both the forward photo-current and the rectification ratio were markedly improved when the compacted powder of blue-TiO$_2$NWs (reduced, containing Ti$^{3+}$ species) was used as the model ETL as compared to the compacted white-TiO$_2$NWs (thermally re-oxidized).

Thus, for the herein studied model ETL/MHP interface, both the low-temperature Photo-EPR measurements and the results obtained for a simple light detector confirm that blue-TiO$_2$NWs serve as a unidirectional electron sink with an enhanced electron trapping efficiency due to the presence of Ti$^{3+}$ species.

Overall, we also infer that the technique of low-temperature Photo-EPR is an effective strategy to study the transfer mechanisms of photogenerated carriers at the ETL/MHP interface in MAPbI$_3$-based photovoltaic and photoelectronic systems.

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