Cascade charge transfer enabled by incorporating edge-enriched graphene nanoribbons for mesostructured perovskite solar cells with enhanced performance

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ABSTRACT

The ability to facilitate charge transfer in electron transport layer (ETL) is highly desirable for high-efficiency perovskite solar cells (PSCs). Herein, we report the judicious design of ETL composed of edge-enriched graphene nanoribbons (GNRs) and TiO\textsubscript{2} nanocrystals to enable markedly improved charge carrier conductivity and, more importantly, well-aligned energy levels at the perovskite/ETL/fluorine doped tin oxide (FTO) interfaces for imparting the cascade charge transfer, thereby leading to improved power conversion efficiency (PCE) of PSCs. The investigation into the influence of the GNR content within ETL on device performance demonstrated that excessive GNRs are detrimental for charge transfer as they block the contact between TiO\textsubscript{2} and perovskite. In contrast to devices using pure TiO\textsubscript{2} as ETL with a PCE of 15.87%, the PSCs employing GNRs-incorporated ETL display the improved photovoltaic performance with a highest PCE of 17.69%, a steady-state efficiency output of 17.05%, and a reduced current-voltage hysteresis. Subsequently, a systematic photo-carrier dynamics study revealed that the performance enhancement was a direct consequence of (a) the promoted fill factor and open circuit voltage due to the improved electron diffusion coefficient and the longer charge recombination time, (b) the increased charge collection efficiency owing to the cascade charge transfer from TiO\textsubscript{2} to GNRs to FTO electrode, resulting in a higher external quantum efficiency and thus a larger short circuit current density and (c) the suppressed current-voltage hysteresis ascribed to the increased charge transfer noted above. Finally, a markedly improved long-term stability was manifested. As such, the rational incorporation of edge-enriched GNRs represents a feasible and robust strategy to formulate promising ETLs for high-efficiency and stable PSCs.

1. Introduction

The past decade has witnessed growing interest in perovskite (ABX\textsubscript{3}; where A = Cs\textsuperscript{+}, methylammonium (MA\textsuperscript{+}), formamidinium (FA\textsuperscript{+}), etc., B\textsuperscript{2+} = Pb\textsuperscript{2+}, Sn\textsuperscript{2+}, etc., and X\textsuperscript{−} = Cl\textsuperscript{−}, Br\textsuperscript{−}, and I\textsuperscript{−}) materials and devices owing to their attractive optoelectronic attributes such as tunable direct band gaps, large absorption coefficient, high ambipolar mobility, high defect tolerance, and solution processability [1–5]. Among various types of solar cells, perovskite solar cells (PSCs) have garnered tremendous interest due to their high power conversion efficiency (PCE), good processability, and low cost. Recently, a highest certified PCE of 22.1% for mesostructured PSCs (m-PSCs) has been reported by introducing additional iodide into precursor solution of perovskite to decrease deep-level defects (e.g., cation or halide vacancies, interstitial and antisite defects, etc.) [6]. When the mixed-cation and mixed-halide perovskites (e.g., FA\textsuperscript{+} mixed with MA\textsuperscript{+} and I\textsuperscript{−} mixed with Br\textsuperscript{−}) are used, PCEs higher above than 20.0% can be achieved in m-PSCs. A typical m-PSC constitutes electron transport layer (ETL) of compact and mesoporous TiO\textsubscript{2}, perovskite layer, and hole transport material (HTM). The TiO\textsubscript{2} layers noted above play vital role in scaffolding perovskite crystals and extracting and transferring photogenerated electrons, imparting high PCE and stable power output.

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of PSCs [7–9]. For CH3NH3PbI3 perovskite, the lowest unoccupied molecular orbital (LUMO) energy level is approximately −3.9 eV vs. vacuum, which is much close to the conduction band (CB) of TiO2 (ca., −4.0 eV) [10], thus facilitating the extraction of photo-induced electrons from perovskite to TiO2. However, the intrinsically poor conductivity (ca., 1.1 × 10−5 S cm−1) of TiO2 and large energy barrier between the CB of TiO2 and the work function of fluorine-doped tin oxide (FTO; ca., −4.7 eV) [11] impairs the efficient electron transfer, thereby leading to inevitable charge accumulation within perovskite and thus charge recombination. This in turn results in serious photocurrent–photovoltage hysteresis and adversely affects the photovoltaic performance of PSCs [12]. Clearly, it is of key importance to design the efficient ETL material for high-performance PSCs. To date, some impressive methods have been developed to engineer ETLs with high charge transfer capability, including tuning the energy-level structure of TiO2 via doping with metal atoms (e.g., yttrium-doped [13] or niobic-doped [14] TiO2) and constructing one-dimensional TiO2 nanocrystals [15,16]. In spite of these effective approaches, the scarcity and high cost of metallic dopants in conjunction with time-consuming preparative procedures for the ETL layer largely restricts practical applications of PSCs. As such, the ability to develop an economically viable strategy for producing highly efficient ETL materials to ensure commendable suppression of charge recombination in PSCs still remains challenging.

Carbon nanotubes (CNTs) have been extensively studied over the past two decades because of their unique physicochemical properties such as high electrochemical stability, excellent conductivity, etc. [17,18]. It has been demonstrated that the basal-plane-like sidewall of CNTs possesses a lower charge transfer rate than that of the edge-plane-like tube ends, thereby affecting the bulk electrochemical activities of CNTs [19,20]. To this end, in order to improve the electrochemical properties of CNTs, a compelling route to high-yield graphene nanoribbons (GNRs) with rich edge sites was developed via longitudinal unzipping of CNTs in oxidative acid solution [21]. Unlike one-dimensional (1D) CNTs, two-dimensional (2D) GNRs have high surface area, expose abundant electrochemically active edge sites, and contact well with nanoparticles, thus rendering them as intriguing materials for use in energy conversion and storage [22,23].

Herein, we report, for the first time, the implementation of edge-enriched GNRs within TiO2 to yield a homogeneous high-quality ETL for low-cost fabrication of mesostructured PSCs (m-PSCs) with enhanced performance via effectively transporting charge carriers and reducing the charge recombination. By judicious incorporation of GNRs into TiO2, the conductivity of the resulting ETL is greatly improved compared with the pure TiO2 ETL, representing a reduced series resistance ($R_s$). On the other hand, GNRs exhibit a work function ($W_{GNRs}$) of −4.3 eV measured by ultraviolet photoelectron spectroscopy (UPS), displaying a well-aligned energy level with respect to that of FTO ($W_{FTO}$ = −4.7 eV) and TiO2 (CB: −4.0 eV). This clearly suggests that GNRs are competent to enable a cascade interfacial charge transfer from TiO2 to GNRs to FTO in m-PSCs, which is instrumental to increase the shunt resistance and retard the charge recombination. The influence of the GNRs content in ETL on the photovoltaic performance of the resulting m-PSCs was investigated by photocurrent density–voltage curves and steady-state photoluminescence (PL) measurements. Subsequently, the charge transfer process within m-PSCs capitalizing on GNRs-incorporated TiO2 was thoroughly explored. In comparison with m-PSC using pure TiO2 ETL (highest PCE = 15.87%), the device based on GNRs-containing ETL yields increased short-current density ($J_sc$) and open circuit voltage ($V_{oc}$) and thus higher PCE (17.69%; a steady-state PCE output of 17.05%) as well as greatly reduced current-voltage hysteresis. Finally, a notably improved stability of m-PSC over pure TiO2 ETL-based device (a 13.3% compared to 47.2% decrease in PCE over a month without encapsulation) was demonstrated, suggesting its potential for practical applications in PSCs.

2. Experimental section

2.1. Preparation of GNRs-incorporated TiO2 slurries

GNRs ethanol suspension was added into TiO2 (19 wt%, 18NR-T) ethanol slurry at different mass fractions (GNRs% = 0, 0.5, 1.3, 2.7, and 4.0 wt%).

2.2. Preparation of graphene nanoribbons (GNRs)

Compact TiO2 layer (denoted c-TiO2) was first prepared on the FTO substrate by spin-coating 0.15 M TiO(acac)2–1-butanol solution containing 0.15 wt% GNRs at 2000 rpm for 30 s, followed by annealing at 125 °C for 10 min. The substrate was then calcinated at 500 °C for 30 min under nitrogen atmosphere. The as-obtained FTO substrate/(c-TiO2/GNRs) was then immersed in 40 mM TiCl4 aqueous solution at 70 °C for 30 min, rinsed with deionized water and ethanol. It was then treated with oxygen plasma. The GNRs-incorporated TiO2 slurries with various GNRs contents were spun on the surface of TiCl4-treated FTO substrate/(c-TiO2/GNRs) at 2000 rpm for 5 s and kept at 125 °C for 10 min. After drying, the resulting FTO substrate/(c-TiO2/GNRs)/(m-TiO2/GNRs) were sintered at 500 °C for 30 min. We note that a mesoporous TiO2 (denoted m-TiO2) was formed from the spin-coating of GNRs-incorporated TiO2 slurries, and the GNRs-incorporated TiO2 ETLs with different GNRs% (i.e., FTO substrate/(c-TiO2/GNRs)/(m-TiO2/GNRs) are denoted GNRs-0.5, GNRs-1.3, GNRs-2.7, and GNRs-4.0 ETLs, respectively. For GNRs-0, it refers to the pure TiO2 ETL containing only c-TiO2 and m-TiO2. Subsequently, the perovskite layer (MAPbI3) was deposited on the FTO substrate/(c-TiO2/GNRs)/(m-TiO2/GNRs) by spin-coating the clear perovskite precursor solution containing 461 mg of PbI2, 159 mg of CH3NH3I, 78 mg of DMSO, and 600 mg DMF at 4000 rpm for 25 s in glove-box, and maintained at 100 °C for 15 min, yielding FTO substrate/(c-TiO2/GNRs)/(m-TiO2/GNRs)/MAPbI3. The hole transport material (HTM) precursor solution, which is composed of 72.3 mg of spiroMeOTAD, 28.8 μL of 4-tert-butyl pyridine, and 17.5 μL of lithium bis(trifluoromethylsulfonyl)imide acetonitrile solution (520 mg/L) in 1 mL of chlorobenzene, was then deposited on the FTO substrate/(c-TiO2/GNRs)/(m-TiO2/GNRs)/MAPbI3 at 3000 rpm for 30 s. Finally, the obtained FTO substrate/(c-TiO2/GNRs)/(m-TiO2/GNRs)/MAPbI3/HTM samples were coated silver electrode with a thickness of approximately 100 nm via thermal evaporation, yielding
the complete device with the architecture of FTO substrate//(c-TiO$_2$/
GNRs)//(m-TiO$_2$/GNRs)//MAPbI$_3$//HTM//Ag. The active area of de-
vice is 0.1 cm$^2$.

2.4. Characterisation

X-ray diffraction patterns were recorded using X-ray diffractometer
(D/Max 2400, RIGAKU, Japan) with Cu K$_\alpha$ radiation (\(\lambda = 1.5406\ \text{\textmu}\text{m}\)).
The measurements were performed using X-ray micro-
scope (Thermo Scientific, USA). The morphologies of samples were
imaged by scanning electron microscopy (SEM, FEI Quanta 450, USA)
and transmission electron microscopy (TEM, Philips Tecnai G220,
USA). The BET specific areas of as-made samples were mea-
sured by N$_2$ adsorption (Micromeritics ASAP 2020, USA). The chemical
composition was examined by X-ray photoelectron spectroscopy with
Al K$_\alpha$ X-ray radiation (XPS, Thermo ESCALAB 250, USA). UV–vis
spectroscopy was conducted using a Shimadzu UV2600 spectro-
photometer with a photometric integrating sphere. Ultraviolet photo-
electron spectroscopy (UPS) of GNRs was determined by a Kratos Axis
Ultra XPS system. The photocurrent density-voltage (J-V) curves were
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3. Results and discussion

Fig. 1a depicts the preparation procedures of GNRs. Specifically,
CNTs were first unzipped along their long axis via chemical oxidation,
yielding graphene oxide nanoribbons (GONRs) with rich edge sites.
The subsequent calcination of GONRs at 900 °C in argon atmosphere pro-
duced GNRs with a small content of oxygen-containing functional
groups. Fig. 1b and c compare X-ray diffraction (XRD) patterns and
Raman spectra of pristine CNTs, GONRs, and GNRs, respectively. The pristine
CNTs shows a strong characteristic diffraction peak at 2θ of
26.0°, which is indexed to the (002) plane. After chemically unzipping of
CNTs, the (002) peak disappears. A new diffraction peak at 2θ of
10.7°, corresponding to the (001) plane of GONRs, appears after un-
zipping, suggesting that considerable defects are introduced in the
GNR matrix such as abundant edge planes and oxygen-containing
functional groups.[24] After calcination of GONRs to obtain GNRs, the
(002) plane shows a larger full-width-at-half-maximum (FWHM) than
that of pristine CNTs, signifying the formation of thinner carbon sheets,
which is favorable due to the high specific area. Moreover, the dis-
appearance of the (001) diffraction peak in GNRs clearly demonstrates
the removal of most oxygen-containing defects.[26]

Raman spectra of CNTs, GONRs, and GNRs display two peaks at
approximately 1350 cm$^{-1}$ and 1590 cm$^{-1}$, which can be assigned to the
D and G bands, respectively (Fig. 1c). The D band is generally related to
structural defects or edges within the carbon matrix, and G band is the
radial C-C stretching mode of sp$^2$ hybridized C rings.[27] The intensity
ratio of D band to G band (I_d/I_g) is commonly used to evaluate the
degree of defects and edge sites in graphitized carbon materials
[26,28]. The I_d/I_g of GNRs is 1.26, which is larger than that of pris-
tine CNTs (1.00), indicating the introduction of oxygen-enriched de-
fects and rich edges into GNRs through the oxidative unzipping pro-
cess. Notably, the I_d/I_g of GNRs further increases to 1.35 after high-
temperature annealing, which can be ascribed to the defects in carbon
backbone induced by the loss of atoms during the thermal decom-
position of oxygen-containing groups.[29]

The morphologies of all samples were examined by field-emission
scanning electron microscope (FESEM) and transmission electron mi-
croscope (TEM, Figs. 2 and S1). Fig. 2a and b show the SEM and TEM
images of pristine CNTs, respectively. The diameter of CNTs ranges
from 20 to 50 nm. It is clear that CNTs are successfully unzipped along the
longitudinal direction of CNTs (Fig. 2c and d), displaying abundant
edges and large aspect ratio, which is bene-
ficial for the improvement of
electrochemical properties and the increase of surface area. It is notable
that the shape of GNRs is well retained after the thermal reduction of
GNRs (Fig. 2e), and the wrinkled GNRs are relatively more trans-
parent than GONRs under the electron beam, manifesting that GNRs are
very thin, which correlates well with the large FWHM observed in the
corresponding XRD pattern described above.

To reveal the chemical bond states and chemical composition of the samples, X-ray photoelectron spectroscopy (XPS) measurements were performed (Figs. 3a, S2, and Table S1). The survey XPS spectra show the binding energies of C 1s and O 1s elements at about 284.6 eV and 530.6 eV, respectively. It is noteworthy that the strong peak intensity of O signal and the pronounced O composition (43.97%) for GONRs suggest the existence of plenty of oxygen-related defects including C-O (286.8 eV) and C=O (288.6 eV) as demonstrated by the deconvolution of the corresponding high-resolution C 1s XPS spectrum shown in Fig. S2b. In contrast to GONRs, the C=C configuration (284.6 eV, Fig. S2c) in GNRs becomes dominant and the O content (1.21%) largely decreases, implying the removal of most oxygen-containing defects and improved graphitization, which is advantageous for charge transfer.

The Brunauer-Emmett-Teller (BET) specific surface area of GNRs was investigated (Fig. S3). The N2 adsorption of GNRs increases over a relative pressure ranging from 0.2 to 1.0 P/P0, which can be attributed to the IV isotherm [30]. The BET specific surface area of GNRs is 325.5 m2 g⁻¹, representing an approximately 6.6 times increase over the pristine CNTs (49.6 m2 g⁻¹), which is clearly favorable for contacting with TiO2 nanoparticles when incorporating GNRs into TiO2 ETL for PSCs. To prepare the ETL with different content of GNRs, a GNR ethanol suspension was first added into the TiO2 ethanol slurry at various mass fractions (0, 0.5, 1.3, 2.7, and 4.0 wt%; hereafter these GNRs-incorporated TiO2 ETLs are denoted GNRs-0, GNRs-0.5, GNRs-1.3, GNRs-2.7, and GNRs-4.0, respectively; see Section 2 for more details). With the increase of GNRs content, the color of the resulting GNRs-incorporated TiO2 paste turns darker (Fig. S4). Nonetheless, they show similar absorption in the UV and visible wavelength regions (Fig. S5), revealing that influence of GNRs in ETLs on the optical absorption is negligible and thus does not affect the light absorption of perovskite photoactive layer. Fig. 3b shows the XPS spectra of GNRs-0 and GNRs-1.3 ETL. The peak intensity of C 1s for the GNRs-0 ETL at 284.6 eV is weaker than that of GNRs-1.3 (Fig. S6a), which is consistent with its lower C content (4.82%, Table S2) than GNRs-1.3 (10.11%), confirming the work function (Ws, GNRs) is a crucial parameter as it greatly influences the charge transfer and energy loss within the resulting PSCs. Thus, the ultraviolet photoelectron spectroscopy (UPS) study was carried out to obtain the Ws, GNRs, where the energy was calibrated with respect to the helium I emission (EHe: 21.2 eV). Fig. 3f displays the UPS spectrum, from which the cutoff and Fermi energies are found to be 1.4 eV and 18.3 eV, respectively. According to the equation, EHe − Ws = Efermi −
The GNR-incorporated TiO₂ ETL was employed in mesostructured PSCs (m-PSCs) with the device architecture of FTO//(c-TiO₂/GNRs)//(m-TiO₂/GNRs)//MAPbI₃//HTM//Ag, as illustrated in Fig. 4a, where c-TiO₂ and m-TiO₂ refer to the compact and mesoporous TiO₂ layers, respectively. Both TiO₂ layers were loaded with GNRs (i.e., ETL), where c-TiO₂ layer contains a fixed amount of GNRs (0.15 wt%) while m-TiO₂ layer comprises a varied amount of GNRs as described above (see Section 2). Spiro-MeOTAD was used as the HTM. Typically, c-TiO₂/GNRs and m-TiO₂/GNRs layers were prepared by spin-coating the respective precursors. MAPbI₃ perovskite was then coated on the (c-TiO₂/GNRs)//(m-TiO₂/GNRs) ETL via one-step deposition followed by anti-solvent treatment and annealing [32]. The spiroMeOTAD layer was introduced on the perovskite film after cooling down to room temperature. Finally, Ag was thermally evaporated on the top of spiroMeOTAD as cathode (Section 2). Fig. 4b and Fig. S8 present the representative cross-sectional SEM image and the corresponding element mappings of the assembled m-PSC, respectively. Clearly, a uniform (c-TiO₂/GNRs)//(m-TiO₂/GNRs) ETL with a thickness of ca. 150 nm is observed. A 300-nm thick, compact perovskite film was formed atop the ETL, and the spiroMeOTAD HTM and Ag layers can also be readily seen.

Fig. 4c depicts the schematic of energy level diagram of various functional layers in m-PSC, where the reported band values of FTO, TiO₂, MAPbI₃, and HTM are used [33]. As noted above, the $W_s,\text{GNRs}$ of GNRs in ETL locates between the $W_s,\text{FTO}$ of FTO and the CB of TiO₂. Thus, GNRs function as bridge to enable a rapid charge transfer from TiO₂ to GNR to FTO in a cascade manner, and markedly reduce charge recombination.

Figs. 4d and S9 summarize the photovoltaic performance of m-PSCs under illumination of AM 1.5G (100 mW cm⁻²) by capitalizing on GNRs.
Fig. 4. (a) Schematic illustration of device architecture. (b) Cross-sectional SEM image and (c) energy level diagram of m-PSC with GNRs incorporated into TiO2 ETL. (d) Power conversion efficiency (PCE) of m-PSCs using different ETLs with a varied amount of GNRs incorporated.

Fig. 5. (a) J-V curves of the champion devices with GNRs-0 and GNRs-1.3 ETLs measured in the reverse scan at a scan rate of 52 mV s\(^{-1}\). (b) Stabilized photocurrent density and PCE as a function of time at 0.80 V for m-PSCs with GNRs-1.3 ETL. (c) EQE spectra of devices with GNRs-0 and GNRs-1.3 ETLs. (d) Steady-state PL spectra of perovskite films on GNRs-0 and GNRs-1.3 ETLs. (e) EIS spectra obtained under dark condition at a bias of 0.8 V (inset: the magnified plot and the equivalent circuit). (f) \(V_{oc}\) decay curves of m-PSCs with GNRs-0 and GNRs-1.3 ETLs.
with different contents in m-TiO2 ETL. The corresponding \(J_{sc}, V_{oc}, FF,\) and PCE are listed in Table S3. Each box represents the distribution of photovoltaic parameters of 15 devices tested under the same working conditions. It is found that the average \(J_{sc}\) of m-PSCs increases with the increasing content of GNRs in ETLs. An optimal average value of 22.89 mA cm\(^{-2}\) is achieved using 1.3 wt% GNRs (i.e., GNRs-1.3), which is higher than that of device without GNRs (GNRs-0, 21.89 mA cm\(^{-2}\)), thus signifying facilitated charge transfer capability of GNRs within ETL. Subsequently, the average \(J_{sc}\) decreases gradually with a further increased GNR loading. At the content of GNRs of 4.0 wt%, the average \(J_{sc}\) declines to 21.23 mA cm\(^{-2}\). Similar trends are also observed for the respective \(V_{oc}, FF,\) and PCE. This will be discussed later. The m-PSC with the optimized addition of GNRs (i.e., 1.3 wt%) yields much improved PCE (average value of 16.87%) compared to that of 14.72% for pure TiO2 as ETL, demonstrating the benefits of introducing GNRs into ETL in minimizing energy loss and enhancing the performance of m-PSCs.

Fig. 5a compares the photocurrent density-voltage (J-V) curves of the champion devices incorporating GNRs-0 and GNRs-1.3 ETLs, respectively. The corresponding photovoltaic parameters are listed as an inset. The champion device with GNRs-1.3 shows a \(J_{sc}\) of 22.98 mA cm\(^{-2}\), a \(V_{oc}\) of 1.053 V, and a FF of 73.1%, and thus a PCE of 17.69%. It is well-known that charge accumulation in the ETL and perovskite can lead to anomalous hysteresis [34–36], which is detrimental for PSCs. It has been reported that the introduction of a fullerene derivative layer with a robust electron extraction ability into PSCs largely reduces the device hysteresis [37]. In this context, the hysteresis behavior of m-PSCs incorporating GNRs-0 and GNRs-1.3 were studied and summarized in Table S4. The difference factor accounting for the difference between PCE achieved via forward scan and reverse scan can be calculated by the following equation: difference factor = \((PCE_{ES} - PCE_{RS})/PCE_{ES}\), where \(PCE_{ES}\) and \(PCE_{RS}\) are the corresponding PCEs obtained from the reverse scan and forward scan, respectively [38]. Clearly, the device with GNRs-1.3 ETL exhibits a much smaller difference factor (6.99%) than that of device with GNRs-0 ETL (13.48%). The smaller difference factor suggests the promoted charge transfer of the GNRs-1.3 ETL and reduced charge recombination. We further measured the stabilized output of device with GNRs-1.3 at fixed bias voltages over 100 s under the standard illumination (AM 1.5G) (Fig. 5b), which exhibits a steady-state current density of 21.31 mA cm\(^{-2}\) and PCE of 17.05%. Ex- under the standard illumination (AM 1.5G) (Fig. 5a) bilized output of device with GNRs-1.3 at (6.99%) than that of device with GNRs-0 ETL (13.48%). The smaller content of GNRs of 1.3 wt% than that of device with GNRs-0 decays sharply because of the fast charge recombination. Conversely, a relatively mild decay for cell with GNRs-1.3 is found. The relationship between the \(V_{oc}\) decay time (\(\tau\)) and \(V_{oc}\) can be described by [41]:

\[
\tau = \left(\frac{k_0 V_{oc}}{q}\right)^{1/2},
\]

from which \(k_0\) can be obtained, where \(k_0\) is the Boltzmann constant, \(T\) is the absolute temperature, and \(q\) is the electron charge. Based on this equation, the \(\tau\) can be qualitatively deduced [42]. Therefore, \(\tau\) of PSC with GNRs-1.3 is larger than that of the device with GNRs-0, suggesting the effective retardation of the charge recombination.

We now turn our attention to further uncover the photo-carrier dynamics of m-PSCs constructed without (i.e., GNRs-0) and with GNRs (i.e., GNRs-1.3) as ETL by performing the intensity-modulated photoluminescence spectroscopy (IMPS) studies. In general, IMPS measures the photocurrent as a function of incident illumination intensity at 0 V bias, namely, the short-circuit condition. For example, the \(\eta_{cc}\) of the device with GNRs-1.3 is 1.8 times that of device with GNRs-0, suggesting the photogenerated electrons can diffuse rapidly from perovskite to the FTO substrate, and thus effectively reduce the charge recombination during the charge transport. This trend (i.e., increased \(D_{\pi}\)) is consistent with the reported work on planar perovskite solar cells [44,45].

For the IMVS study, it was performed at the open-circuit conditions. Similar to IMPS, the IMVS measurement also yields a frequency \(f_{IMVS}\), corresponding to the minimum of the Nyquist plots, according to the equation: \(f_{IMVS} = 1/(2\pi\tau_{IMVS})\), where \(\tau_{IMVS}\) is the charge recombination time. Fig. 6e compares the \(\tau_{rec}\) values of two devices using GNRs-0 and GNRs-1.3 ETLs, respectively. Clearly, every semicircle displays a maximum at a certain frequency \(f_{IMPS}\). The electron transport time \(\tau_{tr}\) is inversely proportional to the \(f_{IMPS}\) according to the equation [43]:

\[
\tau_{tr} = \frac{1}{2\pi f_{IMPS}}.
\]

\(\tau_{tr}\) and \(\tau_{rec}\) depict the typical Nyquist plots of IMPS for devices with GNRs-0 and GNRs-1.3 ETLs, respectively. Clearly, every semicircle displays a maximum at a certain frequency \(f_{IMPS}\). The electron transport time \(\tau_{tr}\) is inversely proportional to the \(f_{IMPS}\) according to the equation [43]:

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\tau_{tr} = \frac{1}{2\pi f_{IMPS}}.
\]

\(\tau_{tr}\) and \(\tau_{rec}\) depict the typical Nyquist plots of IMPS for devices with GNRs-0 and GNRs-1.3 ETLs, respectively. Clearly, every semicircle displays a maximum at a certain frequency \(f_{IMPS}\). The electron transport time \(\tau_{tr}\) is inversely proportional to the \(f_{IMPS}\) according to the equation [43]:

\[
\tau_{tr} = \frac{1}{2\pi f_{IMPS}}.
\]
types of sensitizer and the semiconductor photoanode \cite{47}. In this work, the sensitizer is MAPbI$_3$, and the semiconductor is TiO$_2$. Therefore, compared to the GNRs-0-based device, the EQE(λ) of the GNRs-1.3-based device is higher over the wavelength range of 350–850 nm due to higher $\eta_{cc}$, which agrees well with higher integrated $J_{sc}$ shown in Fig. 5c. On the basis of the IMPS and IMVS studies, the following important information is gained. First, the increased FF and $V_{oc}$ for m-PSC with GNRs-1.3 ETL are due to the larger $D_n$ and $\tau_{rec}$ compared to the device without GNRs, thereby efficiently retarding the charge recombination. Second, the EQE of GNRs-1.3-based device is enhanced owing to the increased $\eta_{cc}$, resulting in a larger $J_{sc}$ and thus a higher PCE. Finally, the current-voltage hysteresis of GNRs-1.3-based device is reduced because of a small $\tau_{tr}$, in other words, the charges can be readily transferred at the ETL/FTO interface and eliminate the excessive charge accumulation in the MAPbI$_3$ layer.

As discussed earlier above, as the content of GNRs in ETL increases above 1.3 wt%, the photovoltaic performance decreases, this can be rationalized as follows. Fig. 7a shows the steady-state PL of perovskite MAPbI$_3$ films deposited on GNRs-0.5, GNRs-1.3, GNRs-2.7, GNRs-4.0 ETLs. The peak intensity follows the order of GNRs-1.3 < GNRs-0.5 < GNRs-2.7 < GNRs-4.0, indicating the decreased charge transfer ability at the ETL/perovskite interface, which correlates well with the corresponding photovoltaic performance (Figs. 4d and S9). As the work function of GNRs ($W_s$, GNRs = −4.3 eV) is more negative than the CB of TiO$_2$ (−4.0 eV) and perovskite (−3.9 eV) (Fig. 4c). Thus, the charge

Fig. 6. Nyquist plots of the IMPS studies on devices with (a) GNRs-0 and (b) GNRs-1.3 ETLs. The derived (c) electron transfer time ($\tau_{tr}$) and (d) charge diffusion coefficient (D) as a function of light intensity. The derived (e) charge recombination time ($\tau_{rec}$) and (f) charge collection efficiency ($\eta_{cc}$) as a function of light intensity from the IMVS studies.

Fig. 7. (a) Steady-state PL spectra of perovskite films on different GNRs-incorporated TiO$_2$ ETLs. (b) Possible mechanisms of charge transfer at perovskite/ETL/FTO interfaces for low GNRs content (≤1.3 wt%; left panel) and high GNRs content (>1.3 wt% yet ≤4.0 wt%; right panel), respectively.
extraction of TiO₂ from perovskite is favored over that of GNRs from perovskite due to the lower energy barrier between TiO₂ and perovskite. There are two possible charge transfer mechanisms that may occur, as illustrated in Fig. 7b, respectively. When introducing a small content of GNRs (i.e., ≤ 1.3 wt%), the charge transfer from perovskite to FTO can be easily accomplished due to well-matched energy alignment with GNRs (left panel in Fig. 7b). Conversely, the incorporation of a large content of GNRs into ETLs increases inevitably their contact with perovskite owing to the high BET specific surface area of GNRs, thus hindering the charge extraction (right panel in Fig. 7b) and eventually resulting in decreased device performance.

Long-term stability is crucial for practical applications of PSCs. The organic-inorganic perovskite (e.g., MAPbI₃) is known to suffer from moisture-, oxygen-, heat-, and UV light-induced decomposition, thus largely limiting the durability of devices [48–50]. The stability of unencapsulated devices assembled with GNRs-1.3 and GNRs-0 ETLs and stored in the desiccator were evaluated under ambient condition (temperature: 25 ± 2 °C, relative humidity: 30 ± 5%), and is shown in Fig. 59a. Intrinsically, the m-PSG with GNRs-incorporated TiO₂ exhibits a markedly improved stability in comparison to the m-PSC without GNRs (13.3% decrease in PCE for GNRs-1.3 devices compared to a 47.2% decrease in PCE for GNRs-0 devices over one-month testing).

To address the possible reason for the greatly improved device stability, UV absorption measurements on both GNRs-0 and GNRs-1.3 ETLs were conducted as shown in Fig. 59b. The GNRs-1.3 ETL demonstrates a relatively higher photoreponse in the UV region than the pure TiO₂ ETL (i.e., GNRs-0). The absorption of UV light by GNRs for the device with GNRs-1.3 ETL likely reduces the UV degradation of TiO₂ and perovskite [51] to some extent during the stability test, thereby leading to the improved device stability. Further improvement on the stability of PSCs (e.g., the encapsulation of devices to protect them from being degraded by moisture, oxygen, and UV light; increasing the perovskite complexity; etc.) is currently under investigation.

4. Conclusions

In summary, we developed a robust ETL constructed by incorporating GNRs with rich electrochemically active edges into TiO₂ paste for enabling cascade charge transfer in ETL when capitalizing on them in m-PSCs. The resulting GNRs-incorporated ETLs possess improved conductivity and negligible absorption in visible wavelength region. More importantly, GNRs exhibit an optimal work function, which presents an advantageous energy level that matches with the FTO substrate and the CB of TiO₂, thereby retarding the charge recombination and minimizing the energy loss. When first capitalizing on the GNRs-1.3 ETL into m-PSCs with MAPbI₃ as perovskite photactive layer, an enhanced PCE of 17.69%, a steady-state efficiency output of 17.05%, and a largely reduced current-voltage hysteresis were achieved, outperforming the device with pure TiO₂ ETL. The scrutiny of the effect of the GNRs content within ETL on the photovolatic performance of devices demonstrated that an excessive amount of GNRs within ETLs hinders the charge transfer process due to their high specific surface area blocking the direct contact between perovskite and TiO₂ and thus leading to decreased device performance. Subsequently, a thorough investigation into the photo-carrier dynamics by a combined IMPS and IMVS study revealed that the enhanced performance can be attributed to the following several reasons. First, the FF and Voc are promoted because of the improved ΔD and rsc. Second, the ηrec is increased due to the efficient cascade charge transfer from TiO₂ to GNRs to FTO electrode, leading to higher EQE and Jsc, and in turn higher PCE. Third, the current-voltage hysteresis is greatly suppressed owing to the large ΔFAR, thus the charges can be readily transferred at the ETL/FTO interface and the excessive charge accumulation in perovskite can be avoided. Finally, an improved long-term stability of m-PSC employing GNRs-incorporated ETL was demonstrated. In essence, the loading of GNRs in semiconductors may stand out as a simple, viable and low-cost strategy to effectively transfer charges for high-performance and stable perovskite-based devices.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2018.07.028.
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