Interfaces Between Graphene-Related Materials and MAPbI₃: Insights from First-Principles.

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Abstract

Given the unique and complementary properties of halide perovskites and graphene, it has been a natural step to explore their combination for novel high-performance solar cells. Within this Research News we review the latest theoretical and computational works on interfaces between the prototype perovskite absorber methylammonium lead tri-iodide (CH₃NH₃PbI₃) and graphene related materials (GRMs). In particular, we review recent works based on quantum-mechanical calculations from first-principles that probe the structural and electronic properties of interfaces between CH₃NH₃PbI₃, pristine graphene, graphene-oxide and reduced graphene-oxide. We discuss how these studies investigate the fundamental mechanisms by which GRMs can improve perovskite based photovoltaics, and how these relate to the several available experimental studies that have clearly shown the positive effects of GRMs on both the charge extraction rates, and the stability of perovskite solar cells. Finally, we discuss the main challenges that remain to be addressed in order to model more realistic systems and further unravel the atomic-scale details that underlie the properties of GRM/perovskite interfaces.

1 Introduction

During the past six years lead halide perovskites have revolutionised the field of solution processable solar cells, achieving record power conversion efficiencies (PCE) of more than 22% [1]. One of the key factors to achieve, or even surpass these PCE values, is the effective extraction of charge carrier (electrons and holes) from the light-absorbing perovskite layer. Nowadays TiO_2 and spiro-OmeTAD are the standard material choices for electron and hole transport layers, respectively [2]. In view of further optimising charge carrier extraction while avoiding recombination at the interfaces, several interfacial engineering approaches have been developed [3]. Lead halide perovskites solar cells are known to degrade upon exposure to ambient conditions [4]. In particular, light and moisture are known to accelerate the degradation of the PCE. Many efforts have been focused towards avoiding the degradation of the solar cells by, for example by modifying the perovskite active layer [5] and by employing encapsulating layers [4]. In this context it was also shown that engineering the interface between the perovskites and the charge transport layers increases the lifetime of the photovoltaic devices [6, 7]. Hence interfacial engineering can have beneficial effects on both charge transport and stability of the halide perovskite solar cells.

On a different front, graphene and its related derivatives have attracted enormous interest due to their remarkable mechanical, electronic and optical properties [8]. In fact, graphene-related materials (GRMs) are well-known for being thermally, mechanically and chemically very stable, they can be easily processed into uniform ultra-thin optically transparent layers, and they can also efficiently transport electronic charge carriers [9]. Therefore, these two-dimensional materials have been investigated widely for many opto-electronic applications, such as transistors [10], photovoltaics [11], photodetectors [12], light emitting devices [13], and catalysts [14]. In the case of solar cells, graphene and its derivatives have been investigated extensively as functional layers, such as transparent conductive electrodes, selective contacts, encapsulation layers, or even as a complement to the photo-active material [15].

2 Experimental Findings

Unsurprisingly, significant efforts have been made towards combining halide perovskites with GRMs, with the goal of realizing stable, high performance photovoltaic devices [15]. In one of the first attempts in this direction, Wang et al. [16] reported on the combination of graphene nano-composites with TiO_2 nano-particles for the electron extraction layer in solution-processable perovskite solar cells. They found that the addition of graphene increases the power conversion efficiency (PCE) of the solar cells by 10% as compared

to the devices without graphene, up to a total PCE of 15.6%. The observed performance enhancement was ascribed to the reduction of the series resistance due to the mobility of carriers in graphene, and the increase of the recombination resistance because TiO_2 nano-particles would limit the direct contact between the perovskite and graphene and hence not allow the formation of recombination centers.

In a related work, Zhu et al. [17] introduced a layer of graphene quantum dots at the interface between TiO_2 and the perovskite absorber. The resulting devices achieved a PCE above 10%, higher than the 8.8% PCE of the devices without graphene. By employing ultrafast transient absorption spectroscopy, the authors noted that the electron extraction times decrease from 260-300 ps without graphene to 90-100 ps with graphene. Based on this observation they assigned the increase in efficiency to an improved carrier extraction. Agresti et al. [18] explored the possibility of further improving electron extraction by engineering the energy-level alignment between perovskites and graphene oxide (GO), using Li functionalization. The best solar cells exhibited a PCE enhancement of 1%, as well as increased stability, even in the absence of encapsulation. In a further attempt, Agresti et al. [19] used graphene/mesoscopic- TiO_2 (m- TiO_2) and Li-functionalized GO on the electron collection side. These devices exhibited slightly improved performance, and importantly a three-fold increase of the T_{80} lifetime (this is the time needed for the PCE to drop by 20% of its initial value). Biccari et al. [20] performed a systematic comparison between perovskite solar cells incorporating graphene/m- TiO_2 , Li-functionalized GO/m- TiO_2 , and their combinations [20], and found that graphene also improves the morphology of the perovskite layer, with beneficial consequences for device performance and stability.

Graphene and GO have also been employed for optimizing the performance of halide perovskite solar cells with ZnO as the electron transport layer [21, 22]. In a first attempt Ameen et al., [21] showed that graphene could be used for flexible perovskite solar cells with a PCE of 9% and enhanced electron transfer. Tavakoli et al., [22] used rGO to successfully passivate ZnO nano-particles, enhance electron carrier extraction and efficiently reduce charge carrier recombination. The ZnO/rGO solar cells reached PCE of up to 15% on glass substrates.

GRMs were also employed as hole-transport layer, with the aim of replacing the standard spiro-OmeTAD which is expensive and prone to degradation. Palma et al. [23] used reduced graphene-oxide (rGO) as a hole-transport layer, and successfully demonstrated functional mesoscopic perovskite solar cells with a PCE of 6.6%. Interestingly these cells managed to maintain their PCE even after a 2000h shelf-life test. rGO was also employed as a hole transport layer by Yeo et al. [24], this time in planar perovskite solar cells. The authors found that in addition to improving the PCE, rGO slightly improved the stability of the perovskite layer.

Attempts have been also made to incorporate graphene both on the electron and hole side. Agresti et al. [25] combined graphene with m-TiO₂ to facilitate electron extraction, and GO was added as an interlayer between the perovskite and the hole transport layer spiro-OmeTAD. These devices achieved PCEs above 18%, but the GO/spiro-OmeTAD combination appeared to accelerate degradation.

On a slightly different front, rGO was introduced to prevent the degradation of hole transport material copper(I)thiocyanate (CuSCN), further highlighting the potential of GRMs in high-performance perovskite solar cells [2].

Figure 1: Schematic illustration of the uses of graphene-related materials in halide perovskite solar cells. The list is based on experimental data discussed in Refs. [16–20, 23–25].

A schematic overview of all the reported uses of GRMs as electron or hole transport layers is shown in Figure 1. Overall, experimental evidence shows that graphene-related materials have beneficial effects on the performance of perovskite solar cells, they can increase device stability, and can be processed with low manufacturing costs. [An in-depth review of recent experimental results on combinations of GRMs with perovskites can be found in Ref. \[15\].](#)

In general, computational and theoretical approaches have been employed extensively to unravel key fundamental processes, optimize interfaces, and design new opto-electronic devices with ideal layers. Employing computational approaches offer a way to systematically look at the atomic-scale mechanisms that are often unclear within experiments. Furthermore, theoretical investigations are less expensive than experiments, while at the same time offer great control of the parameters under which the study takes place. Yet, despite the promise of GRMs in perovskite research and the clear advantages provided by computations, we are still lacking detailed investigations of the fundamental properties of the interfaces between halide perovskites and GRMs, and more generally of the interfaces between perovskites and two-dimensional materials. In particular, only a few *ab initio* calculations have been performed in order to elucidate the atomic-scale mechanisms that underlie the observed phenomena at the interfaces between lead halide perovskites and graphene and related two-dimensional materi-

als. In the following we briefly review the latest findings on graphene and graphene-oxide interfaces with MAPbI₃ (MA: methylammonium, CH₃NH₃), which is the archetypal halide perovskite for solar cell applications.

3 Computational Insights

The first step for the computational investigation of the interfaces between the MAPbI₃ and GRMs is to achieve an accurate description of the perovskite surfaces. X-ray diffraction measurements on MAPbI₃ [26] revealed prominent (110) and (001) peaks, suggesting that these surfaces are the most favorable. Haruyama et al. [27] employed first-principles calculations to explore the structural stability, electronic properties, and termination effects of different surfaces of MAPbI₃. In particular, they focused on the tetragonal phase of MAPbI₃, which is known to be the stable phase at room temperature. These calculations showed that the most energetically favorable non-defective terminations are the (110) and (001) surfaces, in agreement with the XRD observations. Between the two possible surface terminations, one exposing a layer of PbI₂ and the other a layer of MAI, it was found that the former is slightly more stable. This result is compatible with the slight iodine and nitrogen under-stoichiometry that was observed in experiments [28].

The next step is to model graphene-related materials. While modelling a pristine graphene monolayer is straightforward, the computational study of graphene oxide and reduced graphene oxide are particularly challenging. The difficulty is primarily related to the structural complexity, as the arrangement of the various functional groups (e.g. epoxies, hydroxyls, carboxyls, carbonyls) on the graphene layer is highly disordered. Moreover, in order to capture realistic arrangements of the functional groups the model systems can become particularly large (i.e. more than 150 atoms). In addition, most experimental studies do not report a detailed characterization of the oxygen content in rGO, making it difficult to perform calculations that can be compared directly to the measurements. A combination of theory and experiments have successfully been employed to investigate the oxygen groups in GO and rGO [29]. However, such level of sophistication is beyond current capabilities in the case of perovskite/GRM interfaces. Furthermore, graphene-related materials that are used in photovoltaic devices are usually ‘few-layer’ thick samples, as opposed to two-dimensional monolayers. Taking these difficulties into account, it is clear that fully realistic *ab initio* calculations of perovskite/GRM interfaces are not yet feasible in practice. Despite these limitations, it is currently possible to perform calculations on idealized models. The use of idealized interface structures is helpful to investigate trends and identify atomic-scale features that assist/prevent charge extraction, that control energy-level alignment, and that underpin the im-

proved stability of perovskites in the presence of GRMs.

In the next part, the discussed models feature the ideal case of graphene, GO or rGO and MAPbI₃ in a planar geometry, and were constructed by employing large commensurate supercells to minimize strains at the interface, as detailed in Refs. [30–33]. Structural optimizations for the interfaces were done within DFT, and the electronic properties were calculated including spin-orbit coupling which are critical for MAPbI₃ [34]. In order to overcome the well-known DFT band gap problem, hybrid functionals like the PBE0 [35] have been employed on the isolated components that form the interface (i.e. pristine graphene, GO, rGO, and bulk MAPbI₃).

3.1 Graphene/MAPbI₃ Interface

The graphene-MAPbI₃ interface was first investigated from first principles by Volonakis and Giustino. [30]. In this work, the most energetically favorable surfaces of MAPbI₃, which are the (110) and (001) with a PbI₂ termination [27], were placed in contact with a pristine graphene monolayer. The optimized atomic models of the interfaces are shown in Figure 2a and b. Structural optimization of the models revealed that the first layer of MAPbI₃ octahedra at the surface tend to rotate along an axis parallel to the interface, as shown in Figure 2c. The net effect is that the degree of octahedral tilt in the MAPbI₃ surface is reduced. This distortion was shown to arise from a redistribution of the electron charge density at the interface, which generates a torque on the Pb-I bonds in such a way as to push the I atoms away from the graphene while attracting the Pb atoms. These effects are shown in Figure 2d and e.

The binding energy between MAPbI₃ and graphene was found to be favoring the formation of the interfaces. For all examined surfaces, the calculated binding energies are larger than 0.3 eV per surface Pb atom, which are in the same range with the reported binding energies of ruthenium dyes on TiO₂ for dye sensitised solar cells [36]. Hence, the interfaces between graphene and MAPbI₃ are expected to be stable. Furthermore, Jiao et al. [31] have additionally explored the case of (001) MAPbI₃ surface with a MAI termination. In this case the binding energy was found to be slightly smaller than the one calculated for the case of PbI₂-termination.

Upon forming an interface between graphene and MAPbI₃, the electronic charge at the interface rearranges, as shown in Figure 3a. We see that electrons accumulate (red isosurface) near the Pb⁺² cations of MAPbI₃, and a depletion layer forms near the graphene sheet (blue isosurface). The resulting interfacial potential step, of the order of 0.3 eV, is expected to assist electron transfer from MAPbI₃ to graphene, and to act as a barrier for photo-generated holes. This picture is consistent with the notion that graphene can act as a selective electron contact for MAPI [15–17]. In addition to the interface dipole, the suppression of the octahedral tilt in the first

Figure 2: (a), (b) Atomistic models of the optimized interfaces between graphene and the (110) and (001) MAPbI₃ surfaces, respectively. (c) Displacement of the atoms within the first surface layer of MAPbI₃, showing the induced rotation of the octahedra. Grey bars indicate the structure prior to optimization. (d) Electron charge rearrangement upon the formation of the interface between graphene and MAPbI₃. The red (blue) isosurface shows electron depletion (accumulation). (e) Forces acting on the atoms near the interface, leading to the suppression of the octahedral tilt in MAPI. Adapted with permission from Ref. [30], Copyright (2015) American Chemical Society.

monolayer of MAPI leads to the establishment of another dipole, this time localized within the MAPbI₃ layer. This effect is linked with the fact that the octahedral rotation breaks the centrosymmetric nature of MAPbI₃, thereby leading to a small ferroelectric effect. The corresponding bulk polarization for the (110) and (001) interfaces is 2.4 mC/m² and 2.9 mC/m², respectively, and is oriented perpendicular to the interface. This dipole is also expected to assist the separation of electrons and holes within MAPI, and may explain the longer recombination lifetimes observed for MAPI/GRMs composites [17]. An illustration of the two dipoles at the graphene/MAPbI₃ interface is shown in Figure 3b.

Hu et al. [32] also used first-principles calculations of the graphene/MAPbI₃ interface. They reported on an alternative graphene/MAPbI₃ stacking arrangement by rotating the graphene layer, and explored the effects of the interlayer distance on the interfacial energy-level alignment. For all the examined stacking arrangements the authors found that electrons accumu-

late near the perovskite layer, thereby creating a charge depletion near the graphene sheet. This is schematically shown in Figure 3c, and corresponds to the same charge rearrangement shown in Figure 3a. Hence, the interfacial dipole that promotes the electron charge transfer from MAPbI₃ to graphene appears to be independent of the stacking configuration, and can be considered as a universal feature of this interface.

A key design parameter for the interface between the charge extraction layers and MAPbI₃ is the energy-level alignment. The *ab initio* calculations of the interfaces between pristine graphene and MAPbI₃ by Volonakis and Giustino, [30] showed that the energy alignment is favourable for electron extraction, with a n-type barrier height of almost 0.7 eV. At the same time, by taking into account the p-type barrier height, the calculations indicate that the maximum open-circuit voltage could be as large as 1.1 eV, at least theoretically. The energy alignment for (110) and (001) interfaces is shown in Figure 3d. It is important to emphasize that, while pure graphene is a zero-gap semimetal, and would therefore act as a recombination layer, the ferroelectric dipole within the MAPI layer could serve to efficiently separate electrons and holes, therefore avoiding that holes reach the graphene sheet. This effect would hinder charge recombination at the interface [30,32]. This scenario is also supported by calculations of the electron wavefunctions at the interface. Indeed it has been shown [30] that the wavefunction corresponding to the highest occupied state of MAPbI₃ is localized away from the graphene layer, while the wavefunctions at the conduction band bottom are located near the interface with graphene. This spatial separation of electrons and holes may prevent electron-hole recombination by suppressing optical matrix elements.

Wang et al., [37] have recently employed first-principles calculations on graphene-MAPbI₃ interfaces to investigate the role of I, Pb, and/or MA vacancies. It was shown that the presence of defects could be detrimental for the performance of MAPbI₃ based solar cells. In particular, I and Pb vacancies at the surface of MAPbI₃, were directly associated with mid-gap electronic levels that would act as deep charge carrier traps, while MA was found to be harmless. Interestingly, the formation of these defects was found to be less energetically favorable at the interface with graphene. Hence, graphene is also expected to have an additional “healing effect” for the interfacial defects.

In summary, first-principles calculations on the graphene-MAPbI₃ interface have been employed successfully to explain the beneficial role of graphene in perovskite solar cells. It was shown that electrons can be extracted efficiently due to a favorable energy level alignment, and that the formation of electrostatic dipoles should promote electron-hole separation and electron transport towards graphene. Moreover, charge recombination at the interface should be hindered by the interfacial dipole and the spatial separation of electrons and holes near the interface. These results led to the

Figure 3: (a) Electronic charge rearrangement at the optimized graphene/MAPbI₃ interface. Red (blue) isosurface shows charge depletion (accumulation). (b) Illustration of the dipoles and the corresponding potential at the interface. Blue arrows depict the interfacial dipole due to the charge rearrangement shown in (a), and red arrows show the induced dipole within the perovskite layer that creates the ferroelectric effect described in Ref. [30]. (c) Schematic diagram of the energy level alignment and interfacial dipole at the MAPbI₃/graphene interface. (d) Calculated energy level alignment for the interfaces between the (110) and (001) MAPbI₃ surfaces and graphene. Adapted with permission from Refs. [30] and [32], Copyrights (2015) American Chemical Society and (2018) Elsevier.

proposal of a new design of solar cells based on a single layer of perovskite and a single layer of graphene, whereby the graphene monolayer would act as both electron transport layer and transparent electrode. [30]

3.2 Graphene-oxide/MAPbI₃ Interface

Moving on from graphene to graphene oxide and reduced graphene oxide, we note that these latter materials have been used extensively as either electron or hole extraction layers [15, 23, 24], but very little is known about the microscopic mechanisms underpinning charge extraction and recombination at the interface. In the following we review a recent computational study aimed at elucidating the properties of the interfaces between halide perovskites and GO/rGO.

Recently Zibouche et al. [33] were able to investigate the effect of dif-

ferent concentration of epoxy groups in GO/MAPbI₃ interfaces. The GO-species were modeled by taking into account only epoxy groups on graphene, which are known to be the dominant oxidation groups in the GO obtained from the Hummers method [29]. Several model interfaces between the PbI₂-terminated (110) surface of MAPI and rGO with an O-content ranging from pure graphene to fully oxidized GO where constructed. An optimized interface for an oxygen content of 66% is shown in Figure 4a. The binding energies of all the interface models considered are positive, and in the same range as for the case of pristine graphene. Therefore it is expected that stable interfaces between MAPbI₃ and rGO can form when the materials are in contact.

Figure 4: Atomistic model of the optimized interface between MAPbI₃ and reduced graphene, for an oxygen concentration of 33% (i.e O:C ratio of 1:6). (b) Calculated interface energy-level alignment for rGO/MAPI interfaces with various O-concentrations. Energy levels are referred to those measured for MAPbI₃ levels [38]. Adapted with permission from Ref. [33], Copyrights (2018) ACS Publishing.

A detailed analysis of the optimized rGO-MAPbI₃ interfaces revealed that, in contrast to the case of pristine graphene, the octahedral tilt in the first layer of MAPbI₃ is not suppressed. This feature was attributed to the less planar nature of rGO, and to the formation of covalent bonds between

the oxygen atoms in rGO and the exposed Pb atoms of MAPbI₃ [33]. As a result, interfaces between MAPI and rGO do not exhibit interfacial ferroelectricity as reported for the MAPbI₃-graphene interface. For example, when MAPbI₃ is interfaced with rGO with 33% of oxygen concentration, the dipole that is induced within the perovskite layer is just 0.2 Debye, compared to 1 Debye calculated for pristine graphene. For the case a fully oxidized GO, the dipole is slightly larger (0.6 Debye) owing to the more uniform distribution of functional groups, which induces a reduction of the octahedral tilt at the surface of MAPbI₃. The interfacial dipole that is formed due the charge rearrangement between the perovskite and rGO/GO layer is also found to be smaller than in the case of pristine graphene. For example, the interfacial dipoles for the interfaces with rGO and GO are below 0.8 Debye, while in the case of graphene the same dipole is as large as 1.4 Debye. Despite these quantitative differences, the direction and sign of the dipole are consistent across these interface models, therefore it is expected that the rGO/MAPI interface will also lead to efficient electron extraction and reduced recombination.

In the same work, Zibouche et al. [33] also report the energy level alignment for the interfaces between MAPbI₃, rGO and GO. The schematic alignment, including the case of pristine graphene, is shown in Figure 4b. All the energy levels reported are aligned to the measured energy levels of MAPbI₃ referred to vacuum [38]. Interestingly the calculations show that, for high O concentration, a type-I straddling heterojunction is formed, with the conduction (valence) band of the GRM layer lying at higher (lower) energies than those of MAPbI₃. In this situation the charge carriers cannot be extracted from the perovskite layer. At low concentration (below 33%), one finds again a type-I straddling heterojunction, however with the band gap of rGO inside the band gap of MAPbI₃. In this case the band alignment permits the extraction of both electrons and holes, however the interfacial dipole discussed above should facilitate electron extraction. [Such energy level alignment is consistent with recent experiments by Agresti et al., \[25\] which showed that low band gap rGO \(i.e. with a low O-concentration\) can enhance hole extraction in the presence of a hole transport layer such as Spiro-OmeTAD.](#) Finally, for oxygen concentrations between 33% and 66% the calculations yield a staggered type-II heterojunction. In this case electron extraction is favored while hole extraction is forbidden, as shown in the inset of Figure 4b. Based on these observations one would expect that rGO layers with intermediate oxygen content should act as selective n-type contacts in MAPbI₃-based perovskite photovoltaics.

4 Conclusions and Outlook

In summary, as graphene, rGO, and GO become more widely adopted in perovskite-based solar cells, it is becoming increasingly more important to understand the microscopic mechanisms that lead to improved efficiency and stability of these composites. Recent theoretical work has helped explaining the improved carrier extraction rates in terms of interfacial dipoles, and the versatility of rGO in terms of the tunable interfacial energy-level alignment. Despite this recent progress, much work remains to be done in order to engineer new perovskite/GRMs solar cells by design. Indeed, in comparison to the significant body of experimental literature on the combination of perovskites and GRMs in solar cells, theoretical investigations are still very scarce. The main reason for such an imbalance is that atomistic models of the interface involve a large number of atoms and many configurations which are equally probable from an energetic standpoint. Furthermore, the charge transport layers in devices are usually mixed with the GRMs, which further complicates computational modelling. Ab initio calculations have been used to probe interfaces between GRMs/TiO₂ [39,40], MAPbI₃/TiO₂ [41,42], and as discussed in this review MAPbI₃/GRMs. However, a realistic description of the ternary interfaces between perovskites and mixed charge transport layers remains currently particularly demanding. Finally, another important difficulty is that most experiments focus on the device level as opposed to the detailed characterization of materials interfaces, and this makes it challenging to validate the theoretical models. As experimental research on MAPI/GRMs composites continues, it will be important to insist on the theoretical and computational modelling of these systems at the atomic scale.

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