Enhanced photon absorption in spiral nanostructured solar cells using layered 2D materials

Mohammad H Tahersima and Volker J Sorger

Department of Electrical and Computer Engineering, The George Washington University, Washington, DC 20052, USA
E-mail: sorger@gwu.edu

Received 2 February 2015, revised 3 June 2015
Accepted for publication 29 June 2015
Published DD MM 2015

Abstract
Recent investigations of semiconducting two-dimensional (2D) transition metal dichalcogenides have provided evidence for strong light absorption relative to its thickness attributed to high density of states. Stacking a combination of metallic, insulating, and semiconducting 2D materials enables functional devices with atomic thicknesses. While photovoltaic cells based on 2D materials have been demonstrated, the reported absorption is still just a few percent of the incident light due to their sub-wavelength thickness leading to low cell efficiencies. Here we show that taking advantage of the mechanical flexibility of 2D materials by rolling a molybdenum disulfide (MoS2)/graphene (Gr)/hexagonal boron nitride stack to a spiral solar cell allows for optical absorption up to 90%. The optical absorption of a 1 μm long hetero-material spiral cell consisting of the aforementioned hetero stack is about 50% stronger compared to a planar MoS2 cell of the same thickness; although the volumetric absorbing material ratio is only 6%. A core–shell structure exhibits enhanced absorption and pronounced absorption peaks with respect to a spiral structure without metallic contacts. We anticipate these results to provide guidance for photonic structures that take advantage of the unique properties of 2D materials in solar energy conversion applications.

Keywords: optical cavity, spiral, nanophotonics, photovoltaics, 2D materials, graphene, transition metal dichalcogenides

Introduction
Widely installed materials for solar cells are amorphous, poly or single crystalline Silicon, and more recently II–VI semiconductors such as cadmium telluride. Both have been widely studied and utilized in the photovoltaic industry. The recent isolation of two-dimensional (2D) transition metal dichalcogenides [4, 5], and their combination in vertical [1, 6, 9, 24] and horizontal functional systems [7, 8] has provided opportunities to form heterostructures that are attractive candidates for solar energy conversion applications. For instance, group VI transition metal dichalcogenides (TMD) are 2D crystals that can exhibit semiconducting behavior. Such materials are constructed by the formula $MX_2$ ($M =$ metal e.g. Mo or W; $X =$ semiconductor e.g. S, Se, or Te) and are structured such that each layer consists of three atomic planes: a lattice of transition metal atoms sandwiched between two lattice of chalcogenides. There is strong covalent bonding between the atoms within each layer and adjacent layers are held together by weak van der Waals forces. These atomically thin heterostructures of semiconducting TMDs allow for surprisingly strong light–matter–interactions, which can be utilized for harvesting sunlight via absorption and photovoltaic effects [1].

Previously TMD/Gr bilayers of vertical heterostructure stacks were studied to improve photocurrent extraction [1, 9, 24] in photovoltaic and photodetector applications.
These heterostructures can utilize effective combination of good solar spectrum absorption of some TMDs such as MoS$_2$ and superior mobility of graphene (i.e. $200,000 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for suspended graphene [18]) in Schottky barrier solar cells. Although a few layers of both graphene and MoS$_2$ are visually transparent, they are promising sunlight absorbers due to their large absorption per thickness and high density of states. Classically the amount of light absorbed in flat photovoltaic cells is proportional to the film thickness. However, creating an increased optical path length significantly reduces the amount of required photoactive materials. This can be achieved via light management architectures such as planar metamaterial light-directing structures, Mie scattering surface nanostructures, metal-dielectric-metal waveguide or semiconductor-dielectric-semiconductor slot waveguides [21]. Here we investigate a three-dimensional, non-bulk solar cell structure based on a variety of stacked 2D materials each with a functional purpose (figures 1(a) and (b)); by rolling a stack of graphene, semiconducting MoS$_2$, and an electrically insulating 2D material. This structure creates an absorbing cylinder forming a light-concentrating optical cavity as we discuss below. This structure is motivated by deploying the mechanical flexibility of 2D materials to enable a multilayer solar cell without the necessity to contact each of the layers separately. The electronic barrier layer needs to be flexible, wide bandgap, and optically transparent insulator to prevent electron and holes generated in a MoS$_2$/Gr heterojunction from recombining in their adjacent stacked layer. Hexagonal boron nitride (hBN) is employed as barrier layer since it is an isomorph of graphene, optically transparent, electrically an insulator with a wide bandgap of about 5.9 eV, and it reduces the traps of MoS$_2$ layers indicated by improved mobilities [6]. A trilayer MoS$_2$ with a bandgap of 1.6 eV [11] was chosen over a monolayer since optical absorption linearly increases with number of layers, and bulk behavior is expected to emerge beyond stacking 3–4 monolayers [9, 19], whereas mobility improves with the number of layers [6]. This translates into, a trilayer MoS$_2$ showing a three-fold higher absorption over monolayer MoS$_2$, and the added benefit of a higher mobility. In this study we contrast two absorbers, namely, the rolled up Gr/TMD/hBN ‘spiral’ cell (figure 1(a)), and a metal-cladded and metal inner-post ‘core–shell’ cell (figure 1(b)). The reason behind studying both is that as to separate the effect of the material (i.e. TMD) absorption from

Figure 1. (a) Schematic of ‘spiral cell structure’; parameters, $d$, $l$, and $t$ stand for diameter of the roll, length of the cylindrical structure, and thickness of the hBN layer. (b) ‘Core–shell structure’ of the spiral solar cell. Back reflector is connected to the core contact. Gold (aluminum) is chosen as a shell (core) selective contact. (c) Planar MoS$_2$/Gr solar cell converting vertically incident photons into electron–hole pairs.

<table>
<thead>
<tr>
<th>Material</th>
<th>nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>0.5</td>
</tr>
<tr>
<td>MoS$_2$</td>
<td>2</td>
</tr>
<tr>
<td>hBN</td>
<td>$t$</td>
</tr>
<tr>
<td>Gold</td>
<td>30</td>
</tr>
<tr>
<td>Aluminum</td>
<td>25</td>
</tr>
</tbody>
</table>
any optical nano-cavity effects the core–shell device might exhibit. For the latter design, the stack rolls around a core metallic rod and is then coated by another metallic shell, where both metals are the electrical cell’s contacts. The core metallic rod with a low work function (aluminum) is in contact with the graphene, whereas the shell contact with a higher work function (gold) contacts to the MoS2 layer towards establishing selective contacts. In our experiment, we numerically investigate light absorption deploying finite difference time-domain (FDTD) techniques. Comparing this spiral design to previously reported TMD based photovoltaic cells and thick (1 μm) planar MoS2 solar cells, we obtain a relative absorption enhancement which serves as a reference.

### Method

To obtain the absorption efficiency and spectral current density of the spiral cell, we first perform 3D FDTD simulations to solve Maxwell’s equations as a function of time and then execute a Fourier transformation. This strategy was selected for efficiency; the time-domain method covers a wide frequency range in a single simulation run.

A multi-coefficient model was used to represent the complex refractive index of a trilayered MoS2 [11], the Graphene monolayer [12], and hBN [13] (figure S1). Here, the general approach is to send a broadband, normally incident plane wave pulse (300–800 nm) on both spiral structures (figure 1). For angles of incidence larger than zero, the spiral cell is tested under both transverse electric (TE) and transverse magnetic (TM) polarization. Results for an unpolarized source can then be calculated by averaging simulation results of these two orthogonally polarized beams (TE and TM). The length of spiral structure studied are between a minimum value of 0.5 μm and maximum of 3 μm in which absorption approaches its maximum values (87%). Cell diameter range from 100 nm to 2 μm as the effect of hBN thickness on spiral cell is examined. We analyze isolated spiral cells within perfectly matched layers in all directions; and planar cells for which perfectly matched layer in x–y direction and periodic boundary condition in x–y plane is implemented. Note, a perfectly matched layer is assumed in propagation direction to absorb any back reflected waves. Furthermore, a power monitor surrounds the entire cell to obtain the net flow out of the simulation domain in all directions (P_{out}). The light source is placed inside the power analysis volume, right below the structures and parallel to the surface of incidence. Hence the absorption (A) is obtained by A = 1−P_{out}. The absorption per unit volume can be calculated from the divergence of the pointing vector:

\[ P_{abs} = -0.5 \left( \mathbf{\nabla} \cdot \mathbf{P} \right) = -0.5 \omega [\mathbf{E}(\omega)]^2 \varepsilon''(\omega), \]

where \( \omega \) is the angular frequency, \( \varepsilon''(\omega) \) the imaginary part of the permittivity, and \( [\mathbf{E}(\omega)]^2 \) the electric field density. Thus, to calculate the spatial and frequency function of the absorption, we only need to know electric field intensity and imaginary part of the complex refractive index. For a solar cell, of relevance is the current density (J), which requires knowledge of the optical generation rate (G), which is given by

\[ G(\omega) = \frac{P_{abs}}{\hbar \omega} = -\frac{E(\omega)^2 \varepsilon''(\omega)}{2 \hbar}, \]

from which we obtain the spectral current density

\[ J_{sc}(\lambda) = \alpha(\lambda) \text{IQE}(\lambda) \Gamma_{AM1.5} \lambda/1.24, \]

where \( \alpha \) is the absorption efficiency, \( \lambda \) is the wavelength, and \( \Gamma \) is the spectral irradiance of the ASTM 892 standard, AM 1.5 G, corresponding to air mass of 1.5 for a 37° tilted surface at one sun solar intensity (data taken from [14]). We assume that for each photon absorbed, one electron–hole pair is created. In other words, the internal quantum efficiency (IQE) is assumed to be unity. The total short circuit current \( J_{sc} \) is obtained by integrating \( J_{sc}(\lambda) \) over the wavelength range of 300–800 nm, namely

\[ J_{sc} = \int \frac{e \lambda}{hc} \text{IQE}(\lambda) \Gamma_{AM1.5} \lambda \, d\lambda. \]

Optical absorption values, in percentage, are then calculated by taking the ratio of total short circuit current of a cell to the maximum attainable short circuit current.

### Results and discussion

The results of the spectral scan display resonant-like fringes in the absorption spectrum, which we associate to cavity resonances as discussed below (figure 2(b)). We also find a higher visibility for the core–shell cell (with the metal cladding) compared to the spiral design (pure dielectric), which can be understood from the optical field confinement inside the structure. The resonances themselves suggest the cylinder spiral structure resembling a nanowire, and hence exhibiting Fabry–Perot cavity behavior [22, 23]. We confirm the latter via (i) investigating the modal features of this cavity (figures 2(c) and (d)), and (ii) analyzing their frequency profile (figure 3(c)). Regarding (i), the transverse (x–y direction, i.e. \( x \) in figure 2(a)) mode profile indicates a dipole for larger wavelength, which turns into quadruples and doubled-quadruples for blue shifting the resonance wavelength (6–1 in figures 2(c) and (d)). In addition the cavities’ standing waves can be seen in the cross-sectional-longitudinal modal profile (i.e. \( x' \) in figure 2(a)), where the mode spacing decreases with wavelength (figures 2(c) and (d)). The higher Q-factors observed of the core–shell cell relative to the spiral cell are clearly visible in the cross-sectional mode profiles as distinct power density lopes (figure 2(b)). The apparent longitudinal focusing effect might be connected to a changing (i.e. increasing) local effective index as experienced by the wave traveling in positive \( z \). Regarding (ii), analyzing the resonance peak-spacing from figure 2(b) and relating them to the inverse of the cavity length allows to test the Fabry–Perot cavity hypothesis via \( \Delta \lambda = (\lambda^2/2L) (n-\lambda(dn/d\lambda))^{-1} \) where \( L \) is the length of the spiral cell (cavity), \( n \) is the effective refractive index, \( (n-\lambda(dn/d\lambda))^{-1} \) is the group index and \( \lambda \) is the...
wavelength (figure 3(c)). Finding the results along a straight line confirms that the core–shell cell is a nanoscale cavity. This discussion suggests that the spiral structure behaves like a circular dielectric waveguide where the end facets act as reflecting mirrors [15, 16]. Neglecting dispersion, the expression for the mode spacing simplifies to \( m = 2nL/\lambda \) where \( m \) is the mode number (an integer). The spiral cell structure exhibits mode numbers between 5 and 13 that correspond to 9 visible peaks of absorption efficiency (figure 2(b)). This is supported by longitudinal mode profiles recorded by power monitors in figure 2, which demonstrates a higher interference visibility for the core–shell structure for all monitored wavelengths.

The spectral current density of a 1 \( \mu \)m thick planar MoS\(_2\) cell, the spiral cell, and the core–shell structure are compared (figure 3(a)). We find the spectral current density to be higher for the spiral structure over almost the entire investigated wavelength range. This is mainly because spiral structures have lower surface reflection due to lower effective refractive index of spiral structures compared to planar MoS\(_2\) structure. Core–shell structure has even higher absorption efficiency than the spiral cell, because the back reflector at the end of core–shell structure allows for light to pass twice through the absorber. The overall current densities of the planar cell, spiral cell, and core–shell structure integrated over wavelengths of 300–800 nm are 25.5 mA cm\(^{-2}\), 29.5 mA cm\(^{-2}\), and 37.2 mA cm\(^{-2}\) respectively. These current densities are several times higher than reported values for silicon nanowire or planar silicon solar cell with antireflection coating [2, 3]. The current density of the spiral (core–shell) cell shows 16 (46)% enhancement compared to the planar structure which is expected, because the spectral current density is higher for spiral and core–shell structures over almost the entire wavelength.

Note, that although the spiral length (\( l \)) was kept constant (1 \( \mu \)m) this does not imply that the same amount of photocactive material was used; for example in a particular simulation, the thickness of monolayer graphene, trilayer MoS\(_2\), and few layers of hBN are set to 0.5 nm, 2.0 nm and 35.0 nm, respectively; and for the planar cell thickness of MoS\(_2\) is 1 \( \mu \)m. Thus, the absorbing materials (graphene and MoS\(_2\)) occupy only 6% of the total volume of spiral cells. This suggests that the ratio of solar energy absorption to volume of photoactive material was \( \approx 7.67:1 \) compared to a bulk MoS\(_2\) photovoltaic cell of the same size. We name this ratio ‘enhancement’ and define it as

\[
\frac{\alpha_{\text{spiral cell}} - \alpha_{\text{bulk cell}}}{\alpha_{\text{bulk cell}}} = \frac{t_{\text{MoS}_2} + t_{\text{Gr}}}{t_{\text{MoS}_2} + t_{\text{Gr}} + t_{\text{hBN}}},
\]

where \( \alpha \) denotes absorption and \( t \) refers to the respective physical layer thickness. This enhancement is proportional to the absorption efficiency of the cell and thickness of hBN layer. However, increasing the thickness of the hBN layer, decreases this absorption efficiency due to a reduction in the...
amount of absorbing material (figure 4). Hence, to optimize the ratio of absorption enhancement relative to the volume of the photoactive material, the number of core–shell structures with different hBN thicknesses are analyzed (figures 3(b) and 4). For core–shell structures with 5 rings and 500 nm length, the optical absorptions given by the division of total current density absorbed by these cells to total current density of solar spectrum, increase from 50.8 to 72.9, 83.2 and 89.1% as we reduce the hBN thickness from 100 nm to 50, 30, and 10 nm (figure 4(b)). The enhancement reaches its peak value of 762% for an hBN thickness of 40 nm. The enhancement however is optimized to 762% for an hBN thickness of 40 nm. The dielectric field strength of hBN was previously studied to be 7.94 MV cm$^{-1}$ [17], which corresponds to a breakdown voltage of 9 V for a 10 nm thin layer of hBN. This is sufficient to prevent excitons generation to electrically short the cell.

Because of their atomic thickness, the electronic properties of 2D materials are sensitive to perturbations such as induced by strain arising from the rolling process, as required here. It has previously been shown that a linear redshift of 45–120 meV in the optical bandgap per percent of applied strain for monolayer and bilayer MoS$_2$, and a direct-to-indirect transition of the optical bandgap occurs at applied strains larger than 1% for monolayer and bilayers of MoS$_2$ [6, 25, 26]. We can estimate the strain in the MoS$_2$ layer of spiral structure by $\sigma = t/2r$, where $\sigma$ is the strain, $t$ the thickness, and $r$ the bending radius of the substrate (hBN). Here we assume that strain effects for a trilayer are similar to a bilayer of MoS$_2$ and a respective substrate. For a core–shell structure with hBN thickness of 10 nm, the tensile strain values are positive and range from 8% at the first ring to 1% at the tenth ring, since the MoS$_2$ trilayer rolls around the center post. However, in a spiral structure with the same hBN thickness, compressive strain values are negative and range from $-17\%$ at the first ring to $-5\%$ at the tenth ring. These strain values correspond to the indirect bandgap regime of strain except of the first ring of the spiral structure (i.e. $-17\%$ strain), which would render the material effectively metallic [27, 28].

In order to verify the performance of the spiral cell at large angles of incidence (i.e. PV cells without tracking system), we compared the light absorption efficiency at varying angle of incidence measured for both TE and TM polarizations (figure 5). For normal incidence, the absorption efficiencies are essentially identical for both TE and TM mode and equal to that of unpolarized light. This is because the reflection coefficient at normal angle of incidence is about the same for all polarizations (figure 5(a)). However, as the angle of incidence increases up to values near the Brewster’s angle, the reflection decrease for $p$ polarized, and increases for $s$ polarized or unpolarized light. This critical angle depends on the effective index of refraction, which has not only dispersive effects, but is also effected by the mode in which light propagates through the structure. The effective index used in figure 5(b) is 1.9 which corresponds to effective index of the core–shell structure at about 550 nm. The effective index of the core–shell structure ranges from 1.6–2.6 corresponding to wavelengths of 500 nm and 600 nm respectively. Group index

Figure 3. (a) Spectral current density of all three structures. Green, red, and blue curves correspond to figures 1(a)–(c) respectively. $d = 1 \mu m$, $l = 0.8 \mu m$. (b) Optimization of hBN thickness to achieve maximum current density to photoactive material ratio. (c) Longitudinal mode spacing versus inverse nanowire length. The average group index for core–shell, and spiral structures are 5.28 and 3.81 respectively.
of the core–shell structure is about 5.3 which is in range values often observed in plasmonic devices [24].

To report an accurate overall power conversion efficiency of proposed spiral solar cell, a 3D device modeling and simulation with accurate electrical characteristic is inevitable. However, the power conversion efficiency for the investigated spiral core–shell design could be estimated using the short

circuit current obtained in this work, known physical parameters of materials used (table S1). We state a lower and a reasonable limit for this efficiency, and use the current density ($J_{SC}$) of 37.2 mA cm$^{-2}$ for the cell with length of 1 μm and radius of 400 nm. An open circuit voltage ($V_{OC}$) of 0.1 and 0.5 V [9], and fill factor of 0.3 and 0.7, can be estimated as a lower and reasonable limit, respectively. In both cases an IQE

Figure 4. Effect of hBN thickness on the absorption efficiency of spiral structure (a) and core–shell structure (b). The number of rings are set to 5 and length of the spirals are 500 nm. In both structures, reducing hBN thickness leads to increase in absorption efficiency.

Figure 5 (a) Refractive index of the core–shell spiral structure at wavelength of 450 nm. (b) Brewster angle of the core–shell spiral structure with effective index of 1.9 (effective index of structure at 500 nm). Absorption efficiency of the cell with TM (c) and TE (d) polarized source with different incident angles.
of unity and input power \( P_i \) of 1000 W m\(^{-2}\) are assumed. The efficiency \( \eta \) is then calculated from

\[
\eta = \frac{FF \times J_{SC} \times V_{OC}}{P_i}
\]

resulting in an overall power conversion efficiency ranging between 1% and 13%.

**Conclusion**

We have investigated a novel photovoltaic absorber and successfully demonstrated that rolling 2D materials into 3D structures can significantly improve their photo absorption compared to atomically thin or even bulk configurations. The spiral solar cell design can be optimized by tuning the hBN thickness to maximize either the optical absorption (up to 90\%), or the absorption relative to the amount of photoactive material used (up to 762\% enhancement).

The main reason for estimated medium-high power conversion efficiency of 1 to 13\% is the low \( V_{OC} \) and should be the first target of further improving the cell. One possible way to overcome this barrier is to use a multi-stack of 2D materials with different bandgap, such as alloying two materials with different bandgaps such as MoS\(_2\)/WSe\(_2\). Furthermore, recent efforts on designing materials with different bandgap, such as MoS\(_2\)/MoS\(_2\), have shown promising results.

**References**


The layout of this article has not yet been finalized. Therefore this proof may contain columns that are not fully balanced/matched or overlapping text in inline equations; these issues will be resolved once the final corrections have been incorporated.

SQ1
Please be aware that the colour figures in this article will only appear in colour in the online version. If you require colour in the printed journal and have not previously arranged it, please contact the Production Editor now.

We have been provided funding information for this article as below. Please confirm whether this information is correct.
National Science Foundation: NSF 1436330.

Page 7

Q1
References [10 and 20] is listed in the reference list but not cited in the text. Please cite in the text, else delete from the list.

Page 7

Q2
Please check if reference [14] is to a book, journal conference proceedings or other and supply the complete details as appropriate.