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Maximum Possible Open-Circuit Voltages in Atomic-Thin Layered Semiconductors

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Introduction

Since the first report of an atomic-thin two-dimensional (2D) material, graphene, interest in various layered materials has increased enormously. Amongst the widely researched thin 2D materials are semiconductors of transition metal dichalcogenides **(**TMDs) courtesy of their properties such as excellent light-matter interaction properties, quantum-confinement effects, atomic thickness and many others.[1] With such useful properties in mind, different research groups have tried to demonstrate (as a proof-of-concept) monolayer TMDs-based photovoltaic devices (commonly from materials such as WS_2, MoS_2, WSe_2, and $MoSe_2$). However, the efficiency of these monolayer TMD-based devices is still much lower than that of traditional photovoltaic technologies, with their best possible efficiency not known to-date. Open circuit voltage (V_{oc}) is one of the essential parameters that determine the efficiency of solar cells. Thus, quantifying it for these atomic-thin materials can be a step closer towards predicting the ideal performance of these novel devices.

Using optical-based characterisation techniques (micro-photoluminescence (*μ-PL) and μ*-absorbance measurements*)*, via the generalised Planck law of emission we were able to predict the maximum possible V_{oc} values of solar cells fabricated from these atomic-thin semiconductors (WS_2, MoS_2, WSe_2, and $MoSe_2$). Briefly, we quantified quasi-Fermi level splitting ($\Delta\mu$) values between excited electrons and holes of these materials under light illumination according to **Equation 1**.[2-3] From a thermodynamic standpoint, this value reflects the maximum possible V_{oc} that a solar cell fabricated from these monolayers can achieve. In principle, the PL emitted from any semiconductor after excitation follows **Equation 1**.

$$dr_{em}(\hbar\omega) = A(\hbar\omega) \times \frac{(\hbar\omega)^2}{4\pi^2\hbar^3c^2} \times \left[\exp\left(\frac{\hbar\omega - \Delta\mu}{kT}\right) - 1\right]^{-1} \quad 1)$$

where $dr_{em}(\hbar\omega)$ is the photon flux per energy interval, $\hbar$, k and c are the reduced Planck constant, the Boltzmann's constant and the speed of light in the medium that the photons are emitted, respectively. $A(\hbar\omega)$ is the absorbance of the emitting material and $\Delta\mu$ is the chemical potential, i.e. the quasi-Fermi energy splitting, of electron-hole pairs under excitation.

Results and discussions

First, we obtained the monolayers of the TMDs by mechanical exfoliation from the bulk crystals. An optical microscope was used to locate the position of the monolayers on the substrate (**Figure 1a**). Finally, μ-PL (**Figure 1b**) and μ-Raman (**Figure 1c**) measurements were employed to confirm the monolayers. After that, we employed **Equation 1** to derive the average values of $\Delta\mu$ ($\Delta\mu_{average}$) of different monolayer TMDs. From the experimental results, the extracted $\Delta\mu_{average}$ values of WS_2, MoS_2, WSe_2, and $MoSe_2$ monolayers were 1400 ± 5, 1121 ± 7, 1055 ± 5 and 929 ± 5 meV, respectively (**Figure 1d**). In **Figure 1e**, we replot $\Delta\mu_{average}$ versus "Shockley-Queisser limit" of V_{oc} ($V_{oc,S\text{-}Q}$). Also, in **Figure 1f**, we compare the $V_{oc,S\text{-}Q}$ - $\Delta\mu_{average}$ gap among the investigated materials. Smaller values mean closer to the fundamental Shockley-Queisser limit. The $V_{oc,S\text{-}Q}$ value of each material is derived based on its PL peak energy position. From **Figure 1f,** the $V_{oc,S\text{-}Q}$ - $\Delta\mu_{average}$ gap of 1-layer (1L) WS_2 is the smallest among the four TMDs. Moreover, this gap is found to increase with increasing full-width at half-maximums (FWHMs) of the PL spectra from the TMDs. As these 1L TMDs have direct bandgaps, the higher FWHM corresponds to the more disorder and defect states, leading to a bigger gap between $\Delta\mu_{average}$ and $V_{oc,S\text{-}Q}$.

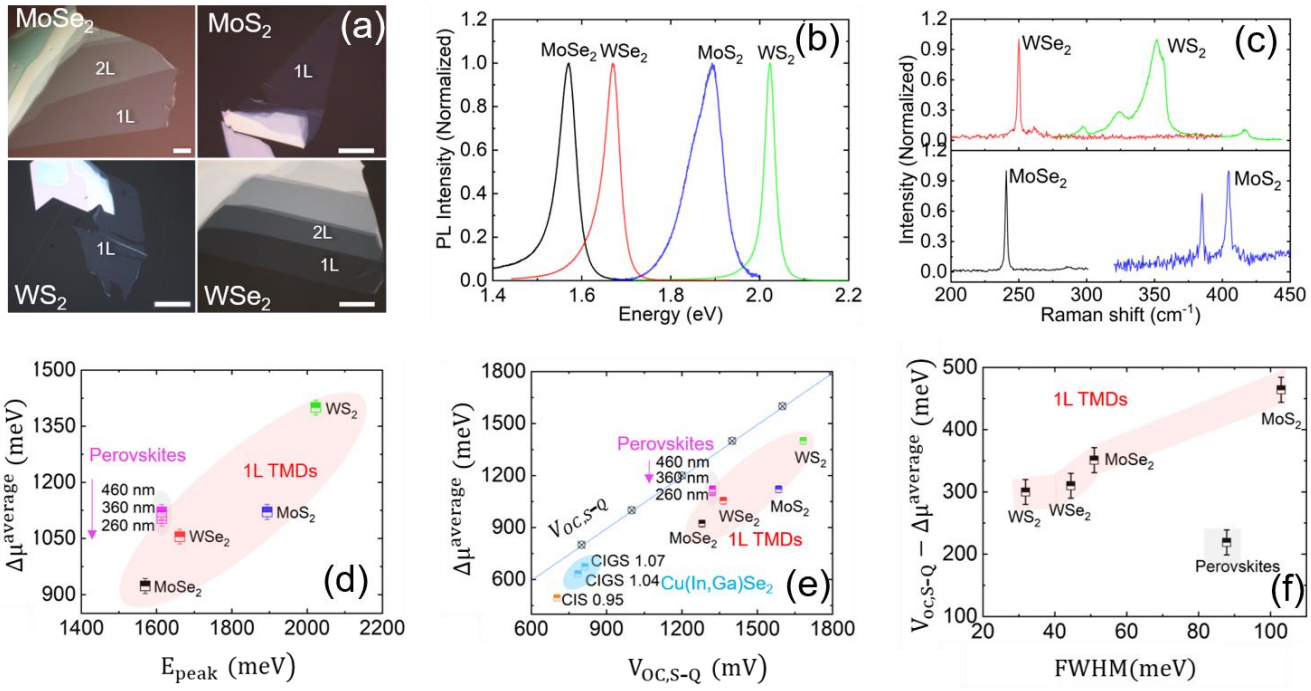

Figure 1. (a) Optical microscope images (the scale bar is 20 μm), (b) PL spectra and (c) Raman spectra of monolayer TMDs. (d) Obtained $\Delta\mu_{average}$ values of monolayers. (e) $\Delta\mu_{average}$ vs $V_{oc,S-Q}$ of TMDs with comparison to other semiconductors and (f) ($V_{oc,S-Q}$ - $\Delta\mu_{average}$) gap versus FWHM of the PL spectra of the monolayers. Images are adapted from Reference 4.

In summary, the obtained quasi-Fermi splitting values, which are considered as the maximum obtainable open-circuit voltage values of atomically-thin TMD-based solar cells, were high (over 1 V). This signifies that the requirements of high voltage, flexibility, ultralight weight, transparency, and stability in future solar cells are possible with atomic-thin monolayer TMDs. The final presentation will explain the underlying physics of the method in details as well as provide comprehensive comparisons among various TMDs, perovskites, and thin-film technologies.

References

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