

Supporting Information:

Physicochemical Characterization of a New Porous 2D Semiconductor Carbon Allotrope, C₁₆: An Investigation via Density Functional Theory and Machine Learning-based Molecular Dynamics

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S1 Power Conversion Efficiency Mathematical Formalism

In this work, we employed two approaches to estimate the power conversion efficiency (PCE): the Shockley–Queisser (SQ) limit^{S1}, which offers a simplified yet idealized estimate,

and the spectroscopy-limited maximum efficiency (SLME) scheme^{S2}, which incorporates material-specific optical properties. Both methods are grounded in the principle of detailed balance between photon absorption and emission in photovoltaic devices.

Below, we summarize the mathematical formalism that underpins these two approaches, following the treatment presented in Ref.^{S3}. The PCE is defined as the ratio between the maximum electrical power density output (P_{PV}) and the total incident power density from the solar spectrum (P_{solar}), and is given by:

$$PCE = \frac{P_{PV}}{P_{solar}}, \quad (1)$$

where

$$P_{solar} = \int_0^{\infty} P(E) dE. \quad (2)$$

$P(E)$ is the global AMG1.5G^{S4} solar energy flux, which is the standard solar spectrum for non-concentrated photovoltaic conversion, taking light absorption and scattering in the atmosphere into account. The output power density is described by the product $J(V)V$, as the maximum output power density (P_{PV}) is obtained maximizing the $J - V$ characteristic of an illuminated solar cell:

$$P_{PV} = J(V_{max})V_{max}, \quad (3)$$

where V_{max} is the voltage that results in the maximum output power density. In this method, the current density, $J(V)$, are described by the following expression:

$$J(V) = J_{sc} - \frac{J_0}{fr} \left(\exp\left(\frac{eV}{k_B T}\right) - 1 \right), \quad (4)$$

where k_B is Boltzmann's constant, e is the elementary charge, fr is the radiative electron-hole recombination fraction and T is the temperature of the solar cell. J_{sc} is the short-circuit current density, also known as the illuminated current or photogenerated current, calculated from the following expression,

$$J_{sc} = e \int_0^{\infty} a(E) \frac{P(E)}{E} dE . \quad (5)$$

$a(E)$ is the absorbance, which is defined as the ratio of power absorbed by the solar device to the power of incident sunlight.

The reverse saturation current density (J_0) is calculated using the detailed balance principle under thermal equilibrium, where the rate of photon emission due to radiative recombination equals the rate of photon absorption from the environment. This condition assumes the solar cell is coupled to an ideal heat sink such that its temperature matches the ambient temperature. Consequently, the surrounding environment is modeled as a black body radiator at temperature T as

$$J_0 = e\pi \int_0^{\infty} a(E) \Phi_{bb}(E) dE , \quad (6)$$

where,

$$\Phi_{bb}(E) = \frac{2E^2}{h^3 v_c^2} \left(e^{\frac{E}{k_B T}} - 1 \right)^{-1} , \quad (7)$$

and h is Planck's constant and v_c is the speed of light.

S1.1 Shockley–Queisser Limit

The absorbance $a(E)$ is modeled as a Heaviside step function in the SQ-limit approximation. This feature means that all photons with energy greater than or equal to the band gap energy (E_g) are fully absorbed, i.e., $a(E) = 1$ for $E \geq E_g$ and $a(E) = 0$ for $E < E_g$. Additionally, this model assumes a radiative recombination fraction $fr = 1$, meaning that radiative recombination is the only loss mechanism and non-radiative processes such as Auger recombination are neglected—even in the case of indirect band gap materials^{S5,S6}.

In this work, the PCE values obtained using the SQ-limit were taken from Rühle's compilation^{S7}, which considers a solar cell operating at 298.15 K, with radiative emission occurring from both the front and rear surfaces of the device. Under this approximation, the only input required from DFT is the fundamental energy band gap, regardless of whether it is direct

or indirect. Excitonic effects can also be incorporated into the SQ-limit framework by replacing the electronic band gap with the optical band gap, defined by the bright excitonic ground-state energy.

S1.2 Spectroscopy Limited Maximum Efficiency

In contrast to the SQ-limit approach, the SLME approximation requires the total absorption coefficient $A(\omega)$ —defined as $A_{xx}(\omega) + A_{yy}(\omega)$ —along with the material thickness Δ and the electronic and optical band gaps. This method also accounts for non-radiative recombination by introducing a radiative recombination fraction fr , modeled using a Boltzmann factor^{S2}:

$$fr = e^{-\frac{\delta}{k_B T}}, \quad (8)$$

where $\delta = E_{op} - E_g$, with E_{op} representing the optical band gap and E_g the fundamental (direct or indirect) electronic band gap.

The absorbance $a(E)$ is evaluated under the same assumptions as the SQ-limit, using the expression^{S2,S8}:

$$a(E) = 1 - e^{-2A(\omega)\Delta}, \quad (9)$$

where $E = \hbar\omega$. Excitonic effects are incorporated both through the total absorption coefficient and in the δ parameter, where the optical band gap E_{op} is replaced by the bright exciton ground-state energy E_X^{br} . In this study, all calculations were performed at a temperature of 298.15 K.

The $SLME_{\max}$ values reported in this work were obtained using the expressions above. However, in this case, the absorbance was approximated by a Heaviside step function, as in the SQ limit. The key distinction lies in the inclusion of the recombination fraction f_r , which differentiates the behavior of direct and indirect band gap semiconductors.

References

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