Supplementary Materials

To accompany

How does graphene enhance the photoelectric conversion efficiency in dye sensitized solar cells? An insight from a theoretical perspective

by

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Figure S1: The structure of dye molecule CC simplified from the dye molecule C219\textsuperscript{[1]}.

Figure S2: The first reference model RM-G: the simplified dye molecule CC was anchored on a 10×6 graphene supercell.

Figure S3: The second reference model RM-T: a molecule CC was anchored on the TiO\textsubscript{2}-(101) surface.
Figure S4: The **RM-GT** interface model before and after optimization, similarly to the reference[^2].

Table S1: The average distance (\(d_{av}\), in Å) and minimum distance (\(d_{min}\), in Å) between the top oxygen atoms and the G sheet in **RM-GT** model.

<table>
<thead>
<tr>
<th></th>
<th>(d_{min})</th>
<th>(d_{max})</th>
<th>(d_{av})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PBE</strong></td>
<td>3.14</td>
<td>3.94</td>
<td>3.54</td>
</tr>
<tr>
<td><strong>PBE-D2</strong></td>
<td>2.55</td>
<td>3.39</td>
<td>2.97</td>
</tr>
</tbody>
</table>

Figure S5: The charge density difference for **RM-GT**. Yellow (green) presents a decrease (increase) of electron density, the result is similar with the reference[^3].
Figure S6: The total and projected DOSs for the Graphene (top), TiO$_2$-(101) slab (middle) and RM-GT (bottom).

Table S2: The relative adsorption energy ($\Delta E = E_C - E_D$) for different hydrogenated positions in RM-G models. Note that C, D and E are the corresponding adsorption positions of the hydrogen atom.

<table>
<thead>
<tr>
<th>H-position</th>
<th>C (RM-G1)</th>
<th>D (RM-G2)</th>
<th>E (RM-G3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E$</td>
<td>0</td>
<td>1.71</td>
<td>3.01</td>
</tr>
</tbody>
</table>

Figure S7: Survival probability curves for electron injections from the LUMO of the molecule CC to the graphene sheets in RM-G1, RM-G2 and RM-G3 systems, respectively.
Figure S8: The absorption spectra of the graphene with dye CC systems are obtained from the TD-BHandHLYP/6-31G(d) level of theory. Note that the labels with character B or N indicate the doped graphene systems by B- or N-dopants, respectively. Note again that the numbers 1 or 2 indicate the link modes of the dye molecule on the graphene layer. In the first mode, the dye molecule is anchored directly on the dopants. The dye molecule is linked on the doped graphene through a carbon vacancy in the second model.

Figure S9: Comparison of the survival probability curves for electron injection from the LUMO of the molecule CC to the substrate graphene sheet or TiO$_2$-(101) slab in RM-T and RM-G1 systems, respectively.
Table S3: The technical setups for the models GT-\(n\), where \(n\) varies from 1 to 6. Note that there are a graphene nano-ribbon in GT-5 and a non-periodic graphene quantum dot in GT-6.

<table>
<thead>
<tr>
<th>Supercell</th>
<th>GT-1</th>
<th>GT-2</th>
<th>GT-3</th>
<th>GT-4</th>
<th>GT-5</th>
<th>GT-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>10x6</td>
<td>10x6</td>
<td>10x6</td>
<td>10x6</td>
<td>13x5</td>
<td>13x7</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>4x4</td>
<td>4x4</td>
<td>4x4</td>
<td>4x4</td>
<td>8x8</td>
<td>8x8</td>
</tr>
<tr>
<td>H saturation</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table S4: The adsorption energy \(E_{\text{ads}}=E_{RM-GT}-E_{\text{CC}}-E_{\text{substrate}}\) for GT-\(n\) (\(n = 1, 2, \ldots, 6\)).

<table>
<thead>
<tr>
<th>GT-1</th>
<th>GT-2</th>
<th>GT-3</th>
<th>GT-4</th>
<th>GT-5</th>
<th>GT-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{\text{ads}}[\text{eV}])</td>
<td>-1.82</td>
<td>-0.98</td>
<td>-8.60</td>
<td>-11.04</td>
<td>-2.40</td>
</tr>
</tbody>
</table>

Figure S10: The time depended survival probability (TDSP) curves of the excited electron on the dye molecule CC during the injection process of the GT-5 and GT-6 models with different distances between CC and TiO\(_2\) surface, respectively. Note that the letters S and L indicate the “short” and “long” distances in the corresponding systems, respectively.

Figure S11: The structure of dye molecule model CBT simplified from the dye molecule C272\([4]\).
Table S5: Mulliken charge number of the oxygen and its neighboring atoms in the models with graphene oxide.

<table>
<thead>
<tr>
<th></th>
<th>O1</th>
<th>O2</th>
<th>O3</th>
<th>Ti1</th>
<th>Ti2</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-O-H</td>
<td>-0.45</td>
<td>-0.60</td>
<td>-0.66</td>
<td>1.45</td>
<td>1.34</td>
</tr>
<tr>
<td>G-OOH-T</td>
<td>-0.54</td>
<td>-0.62</td>
<td>-0.66</td>
<td>1.45</td>
<td>1.35</td>
</tr>
</tbody>
</table>

Table S6: The population number and bond lengths between the oxygen and its neighboring atoms.

<table>
<thead>
<tr>
<th></th>
<th>G-O-T</th>
<th>G-OOH-T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond</td>
<td>O1-Ti1</td>
<td>O2-Ti2</td>
</tr>
<tr>
<td>Population</td>
<td>0.32</td>
<td>0.51</td>
</tr>
<tr>
<td>Length(Å)</td>
<td>2.18</td>
<td>1.86</td>
</tr>
</tbody>
</table>

**Simulations of the Electron Injection**

The time-dependent survival probabilities (TDSP) curves were defined as the probability of the photo-excited electron which is still in the adsorbed dye molecule at time \( t \). Therefore, the TDSP can be computed by applying the time-evolved electronic wave function into the atomic orbitals of the adsorbed dye molecule.

The time-evolved wave function \( \varphi(t) \) can be written as a linear combination of atomic orbitals:

\[
\varphi(t) = \sum_{ij} B_{ij}(t) \varphi_{ij},
\]

where \( \varphi_{ij} \) represents the orbital \( j \) of the \( i \)-th atom. The expansion coefficients \( B_{ij}(t) \), introduced in Eq. (1), can now be computed according to the following equation:

\[
B_{ij}(t) = \sum_k Q_{ij}^k C_k \exp\left(-\frac{i}{\hbar} E_k t\right).
\]

The coefficient \( C_k \) in Eq. (2) is defined by the expansion of the initial state in an orthonormal basis set of \( \varphi(k) \),

\[
\varphi(0) = \sum_k C_k \varphi(k).
\]

The coefficient \( Q_{ij}^k \) in this equation is defined according to the expansion of \( \varphi(k) \) as a linear combination of the atomic orbitals:

\[
\varphi(k) = \sum_j Q_j^k \varphi_j.
\]
The eigenvalue $E_k$ in Eq. (2) can be obtained by solving the extended-Hückel (EH) eigenvalue problem:

$$H Q^k = E_k S Q^k,$$  \(\text{(5)}\)

where $H$ is the EH matrix and $S$ is the overlap matrix in the atomic orbital basis. The non-diagonal Hamiltonian matrix is here determined by the Wolfsberg-Helmholtz constant $K$ and the overlapping matrix element:

$$H_{j,m} = K S_{jm} \frac{H_{jj} + H_{mm}}{2}.$$  \(\text{(6)}\)

Usually, the constant $K$ is set to be 1.75, and the $S_{jm}$ is defined according to the overlap of the atomic orbitals:

$$S_{jm} = \langle \varphi_j | \varphi_m \rangle.$$  \(\text{(7)}\)

Therefore, the projection of the time-evolved electronic wave function onto the atomic orbitals of the adsorbed dye molecular can be obtained as follows:

$$\rho_{MOL}(t) = \left| \sum_j \sum_m B_j^*(t) B_m(t) S_{jm} \right|.$$  \(\text{(8)}\)

Note that the sum over $m$ includes all of the atoms in the research object, whereas the sum over $j$ only includes the atoms in the adsorbed dye molecular.

References:


