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Supplementary Materials

To accompany

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

by

Jian-Ying Xi[a], Ran Jia[*ab], Wei Li[c], Jian Wang[a], Fu-Quan Bai[a], Roberts I. Eglitis[b], and Hong-Xing Zhang*[a]

a. Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, 130023 Changchun, PR China
b. Institute of Solid State Physics, University of Latvia, 8 Kengaraga Str., Riga LV1067, Latvia
c. College of Science, Hunan Agriculture University, 410128 Changsha, PR China

E-mail: jiaran@jlu.edu.cn; zhanghx@jlu.edu.cn
Phone: +86 (0)431 88498962

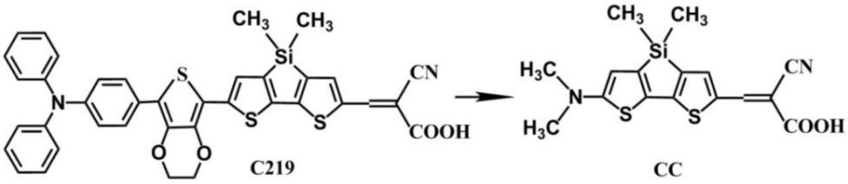

Figure S1: The structure of dye molecule **CC** simplified from the dye molecule **C219**[1].

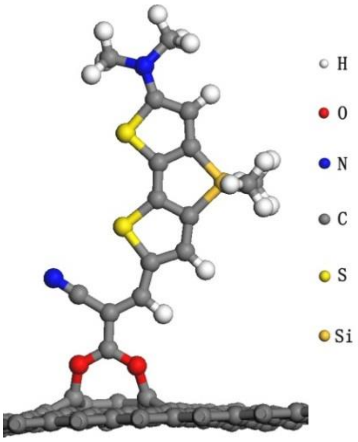

Figure S2: The first reference model **RM-G**: the simplified dye molecule **CC** was anchored on a 10×6 graphene supercell.

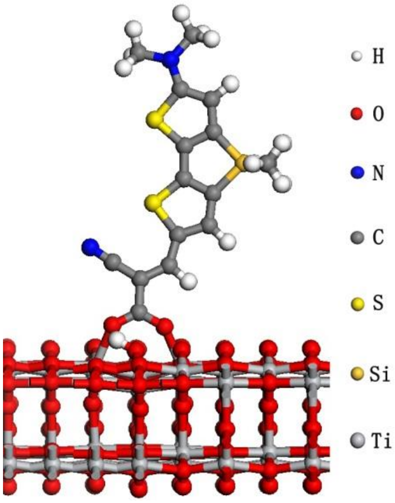

Figure S3: The second reference model **RM-T**: a molecule **CC** was anchored on the TiO_2-(101) surface.

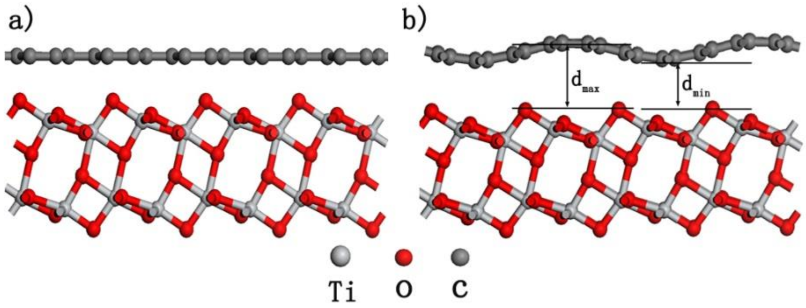

Figure S4: The **RM-GT** interface model before and after optimization, similarly to the reference[2].

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.

	$\mathbf{d_{min}}$	$\mathbf{d_{max}}$	$\mathbf{d_{av}}$
PBE	3.14	3.94	3.54
PBE-D2	2.55	3.39	2.97

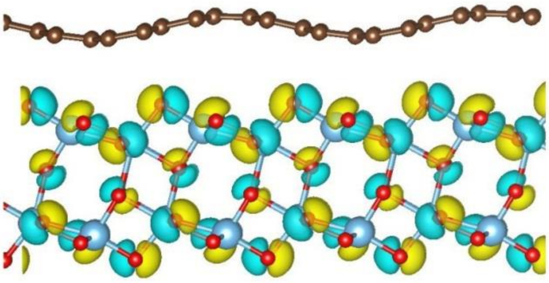

Figure S5: The charge density difference for **RM-GT**. Yellow (green) presents a decrease (increase) of electron density, the result is similar with the reference[3].

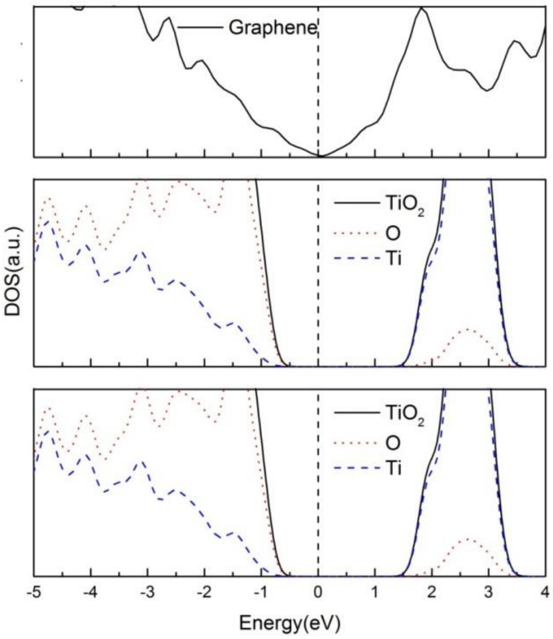

Figure S6: The total and projected DOSs for the Graphene (top), TiO_2-(101) slab (middle) and **RM-GT** (bottom).

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

H-position	C (RM-G1)	D (RM-G2)	E (RM-G3)
ΔE	0	1.71	3.01

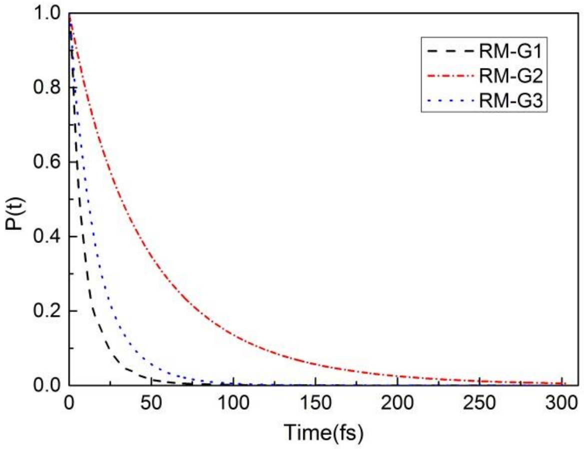

Figure S7: Survival probability curves for electron injections from the LUMO of the molecule **CC** to the graphene sheets in **RM-G1**, **RM-G2** and **RM-G3** systems, respectively.

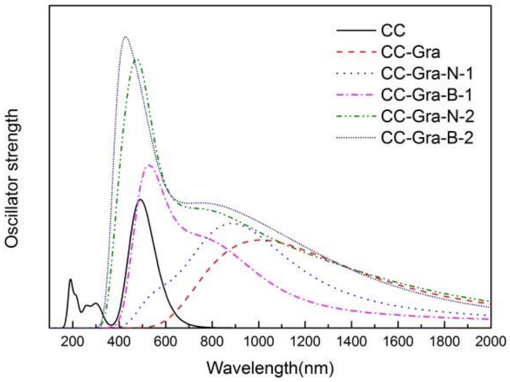

Figure S8: The absorption spectra of the graphene with dye **CC** systems are obtained from the TD-BHandHLYP/6-31G(d) level of theory. Note that the labels with character B or N indicate the doped graphene systems by B- or N-dopants, respectively. Note again that the numbers 1 or 2 indicate the link 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.

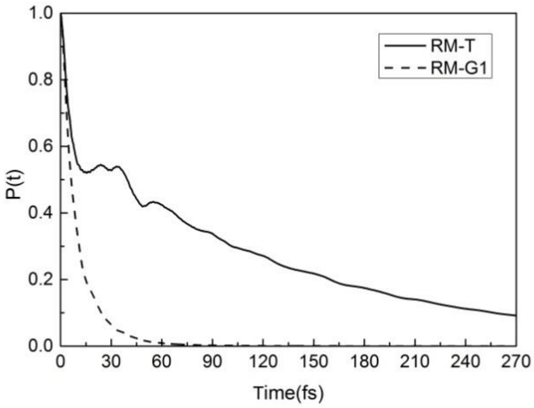

Figure S9: Comparison of the survival probability curves for electron injection from the LUMO of the molecule **CC** to the substrate graphene sheet or TiO_2-(101) slab in **RM-T** and **RM-G1** systems, respectively.

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**.

Supercell	**GT-1**	**GT-2**	**GT-3**	**GT-4**	**GT-5**	**GT-6**
Graphene	10×6	10×6	10×6	10×6	13×5	13×7
TiO_2	4×4	4×4	4×4	4×4	8×8	8×8
H saturation	no	no	no	no	no	yes

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

	GT-1	**GT-2**	**GT-3**	**GT-4**	**GT-5**	**GT-6**
E_{ads}[eV]	-1.82	-0.98	-8.60	-11.04	-2.40	-2.40

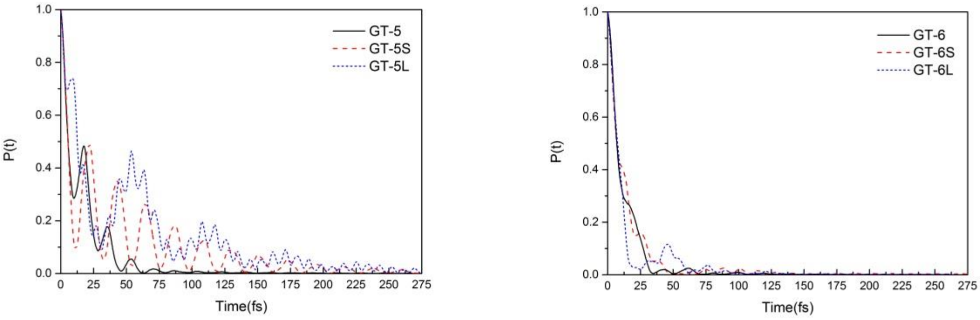

Figure S10: The time depended survival probability (TDSP) curves of the excited electron on the dye molecule **CC** during the injection process of the **GT-5** and **GT-6** models with different distances between **CC** and TiO_2 surface, respectively. Note that the letters S and L indicate the “short” and “long” distances in the corresponding systems, respectively.

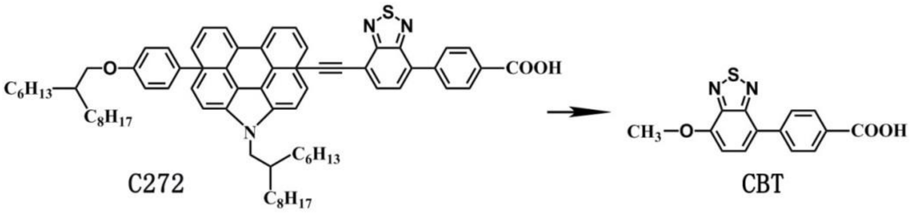

Figure S11: The structure of dye molecule model **CBT** simplified from the dye molecule **C272**[4].

Table S5: Mulliken charge number of the oxygen and its neighboring atoms in the models with graphene oxide.

	O1	O2	O3	Ti1	Ti2
G-O-H	-0.45	-0.60	-0.66	1.45	1.34
G-OOH-T	-0.54	-0.62	-0.66	1.45	1.35

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

	G-O-T			**G-OOH-T**		
Bond	O1-Ti1	O2-Ti2	O3-Ti3	O1-Ti1	O2-Ti2	O3-Ti3
Population	0.32	0.51	0.22	0.57	0.53	0.24
Length(Å)	2.18	1.86	2.05	1.83	1.85	2.04

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 $\varphi(\mathrm{t})$ can be written as a linear combination of atomic orbitals:

$$\varphi(\mathrm{t}) = \sum_{i,j} B_{i,j}(t)\, \emptyset_{i,j}, \tag{1}$$

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

$$B_{i,j}(t) = \sum_k Q_{i,j}^k C_k exp(-\frac{i}{\hbar} E_k t). \tag{2}$$

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

$$\varphi(0) = \sum_k C_k \emptyset(k). \tag{3}$$

The coefficient $Q_{i,j}^k$ in this equation is defined according to the expansion of $\emptyset(\mathrm{k})$ as a linear combination of the atomic orbitals:

$$\emptyset(\mathrm{k}) = \sum_j Q_j^k\, \emptyset_j. \tag{4}$$

The eigenvalue E_k in Eq. (2) can be obtained by solving the extended-Hückel (EH) eigenvalue problem:

$$\mathrm{H}Q^k = E_k S Q^k, \tag{5}$$

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:

$$H_{j,m} = KS_{jm}\frac{H_{jj}+H_{mm}}{2}. \tag{6}$$

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

$$S_{jm} = \langle \varphi_j | \varphi_m \rangle \tag{7}$$

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

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

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:

[1] Zeng, W. D.; Cao, Y. M.; Bai, Y.; Wang, Y. H.; Shi, Y. S.; Zhang, M.; Wang, F. F.; Pan, C. Y.; Wang, P. Efficient dye-sensitized solar cells with an organic photosensitizer featuring orderly conjugated ethylene dioxythiophene and dithienosilole blocks. *Chem. Mater.* **2010**, 22, 1915-1925.

[2] Ferrighi, L.; Fazio, G.; Valentin, C. D. Charge carriers separation at the graphene/(101) anatase TiO_2 interface. *Adv. Mater. Interfaces* **2016**, 3(6):1500624.

[3] Li, X. H.; Gao, H. T.; Liu, G. J. A LDA+U study of the hybrid graphene/anatase TiO_2 nanocomposites: Interfacial properties and visible light response. *Chem. Rev.* **2013**, 1025, 30-34.

[4] Yao, Z. Y.; Wu, H.; Ren, Y. M.; Guo, Y. C.; Wang, P. A, Structurally simple perylene dye with ethynylbenzothiadiazole-benzoic acid as the electron acceptor achieves an over 10% power conversion efficiency. *Energy Environ. Sci.* **2015,** 8, 1438-1442.