Photocatalytic performance of few layer graphitic C$_3$N$_4$: enhanced by interlayer coupling

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The evaluation of hydrogen evolution reaction activity

The hydrogen evolution reaction activity of materials can be evaluated by the reaction free energy of hydrogen adsorption ($\Delta G_H$),$^{1,2}$ defined as

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T \Delta S_H$$

$\Delta E_H$ is the hydrogen adsorption energy

$$\Delta E_H = E_{\text{System+H}} - E_{\text{System}} - \frac{1}{2} E_{H_2}.$$

where $E_{\text{System+H}}$ and $E_{\text{System}}$ are the energies of g-$C_3N_4$ systems with and without H adsorption, respectively. $\Delta E_{ZPE}$ and $\Delta S_H$ are the zero-point energy difference and the entropy difference between the adsorbed and the gas phase, respectively. The $\Delta E_{ZPE}$ can be acquired through vibrational frequency calculation. The $\Delta S_H$ can be taken as $\Delta S_H = \frac{1}{2} S_{H_2}$ because of the fact that the vibrational entropy in the adsorbed state is small on account of previous studies.$^{1,3}$ The optimal value for hydrogen evolution reaction activity is $\Delta G_H = 0$, which means that the smaller values of $\Delta G_H$, the better hydrogen evolution reaction activity performance of materials.

Nonadiabatic molecular dynamics with time-domain density functional theory
We applied *ab initio* nonadiabatic molecular dynamics (NAMD) implemented within time domain density functional theory (DFT) in the Kohn-Sham (KS) framework to model the photogenerated electron dynamics. The Runge-Gross theorem asserts that all observables are determined with the knowledge of the one-body electron density. time domain DFT in the Kohn-Sham approach maps an interacting many-body system onto a system of noninteracting particles where the electron density of the latter equals to the former. The time-dependent charge density of the interacting system can thus be obtained from the time-dependent KS orbitals, $\psi_p(r,t)$ as:

$$\rho(r,t) = \sum_{p=1}^{N_e} |\psi_p(r,t)|^2$$

(1)

The evolution of the electron density is determined by the TD variational principle, leading to a set of single-electron equations for the evolution of the KS orbitals:

$$i\hbar \frac{\partial \psi_p(r,t)}{\partial t} = H(r;R)\psi_p(r,t); p = 1,2,...,N_e$$

(2)

By expanding the time-dependent KS orbitals in the adiabatic KS orbital basis, $\phi_p(r;R)$, which is calculated with time-independent DFT from the geometry in the adiabatic MD as shown below:

$$\psi_p(r,t) = \sum_k c_k(t)\phi_k(r;R)$$

(3)

And by inserting Eq.3 into Eq.2, one can obtain equations for the expanding coefficients:

$$i\hbar \frac{\partial c_j(t)}{\partial t} = \sum_k c_k(t) (\epsilon_j \delta_{jk} + d_{jk})$$

(4)

Where $\epsilon_k$ is the energy of the adiabatic state $k$, and $d_{jk}$ is the non-adiabatic couplings between the basis $j$ and $k$.

The extent of photogenerated electron transfer between active and inactive sites is computed by integrating the projected electron density on active sites (AS).

$$\int_{AS} \rho_{PE}(r,t)dr = \int_{AS} |\psi_{PE}((r),t)|^2 dr = \sum_{i,j} c_i^*(t)c_j(t)\int_{AS} \phi_i^*(r,R(t))\phi_j(r,R(t))dr$$

(5)
Taking the time-derivative of eq (5) gives the expression for adiabatic (AD) and non-adiabatic (NA) contributions to charge transfer:

\[
d\int_{AS} \rho_{PE}(r,t)dr = \sum_{i,j} \left\{ \frac{d(c_i^* c_j)}{dt} \int_{AS} \phi_i^* \phi_j dr + c_i^* c_j \int_{AS} \phi_i^* \phi_j dr \right\}
\]

(6)

The change in the charge density described by the first term on the right-hand side of eq (6) is due to change of state occupations of the adiabatic KS states, which we refer to as nonadiabatic transfer term. On the other hand, the second term causes change of charge density by change of localization of the KS adiabatic states, hence the name adiabatic transfer. The contribution to the total charge transfer was obtained by further integrating the two terms on the right-hand side of eq (6).

**The calculation of binding energy**

In order to determine the interaction between g-C\textsubscript{3}N\textsubscript{4} layers, the binding energy can be calculated by \( E_b = [E_{\text{bilayer}} - (2 \times E_{\text{monolayer}})] / n \), where \( n \) represents the number of atoms, and \( E_{\text{bilayer}} \) and \( E_{\text{monolayer}} \) are the total energies of g-C\textsubscript{3}N\textsubscript{4} bilayer vdW heterostructure, the individual g-C\textsubscript{3}N\textsubscript{4} monolayers, respectively.

**REFERENCES**

Figure S1. The results are obtained by DFT+PBE+TS method. The difference charge density (a) top view and (b) sectional view of bilayer g-C$_3$N$_4$. (c) The bands structure and (d) the imaginary dielectric functions of bilayer g-C$_3$N$_4$.

Figure S2. The results are obtained by DFT+PBE+ dDSC method. The difference charge density (a) top view and (b) sectional view of bilayer g-C$_3$N$_4$. (c) The bands structure and (d) the imaginary dielectric functions of bilayer g-C$_3$N$_4$. 
Figure S3. The results are obtained by DFT+PBE+D2 method. The difference charge density (a) top view and (b) sectional view of bilayer g-C$_3$N$_4$. (c) The bands structure and (d) the imaginary dielectric functions of bilayer g-C$_3$N$_4$.

Figure S4. The results are obtained by DFT+PBE+D3 method. The difference charge density (a) top view and (b) sectional view of bilayer g-C$_3$N$_4$. (c) The bands structure and (d) the imaginary dielectric functions of bilayer g-C$_3$N$_4$.

Figure S5. The interlayer distance of g-C$_3$N$_4$ bilayer.
Figure S6. The interlayer distance of g-C$_3$N$_4$ trilayer.

Figure S7. The interlayer distance of g-C$_3$N$_4$ four layer.
Figure S8. The calculated band dispersion of g-C$_3$N$_4$ (a) monolayer, (b) bilayer, (c) trilayer and (d) four layer based on the DFT-PBE level. The VBM of band structure is set as zero. The band gap is 1.22, 1.70, 1.58 and 1.50 eV for g-C$_3$N$_4$ monolayer, bilayer, trilayer and four layer, respectively.

Figure S9. Calculated imaginary dielectric functions of g-C$_3$N$_4$ monolayer and bilayer for incident light polarization parallel to the surface based on GW+RPA level, compared with the incident solar flux.