Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


**Electronic Supplementary Information**

# Influence of Functional Groups on Water Splitting in Carbon Nanodots and Graphitic Carbon Nitride Composites: A Theoretical Mechanism Study

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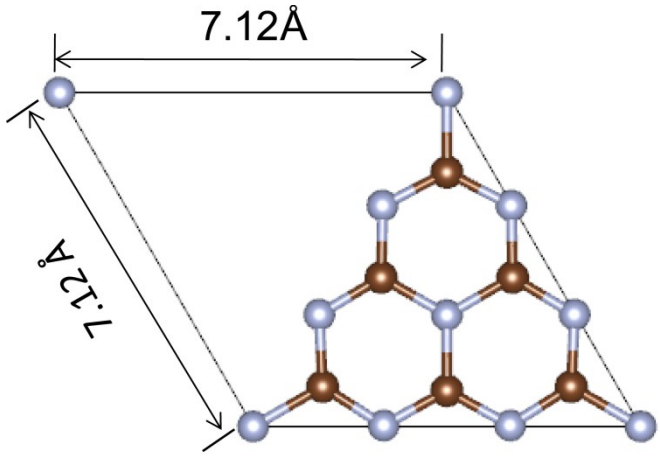


Figure S1. Structure of g-$C_3N_4$ monolayer unit cell.

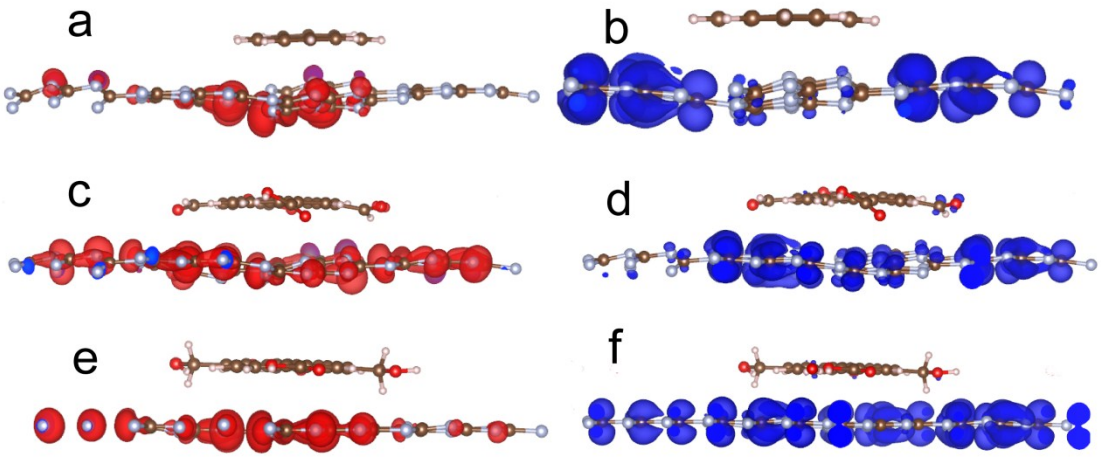


Figure S2. Orbital distributions. a) and b) are VBM-1 and CBM for C-H/g-$C_3N_4$; c) and d) are VBM and CBM+1 for C-CHO/g-$C_3N_4$; e) and f) are VBM and CBM for C-OH/g-$C_3N_4$.

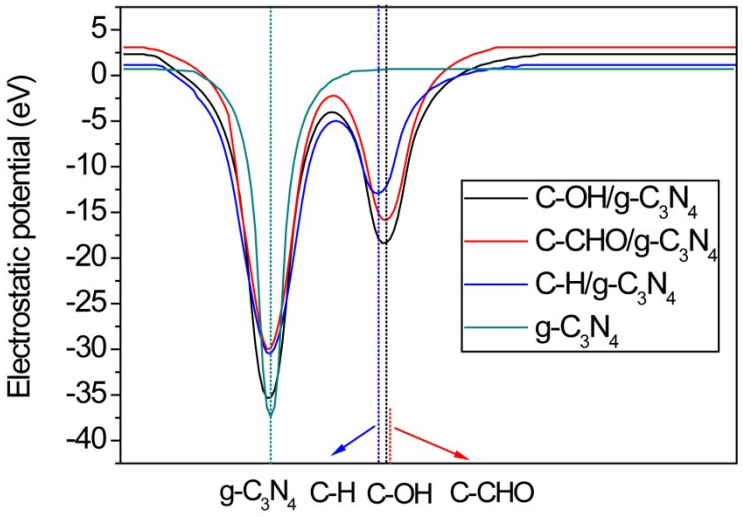


Figure S3. Calculated planar averaged electrostatic potential.

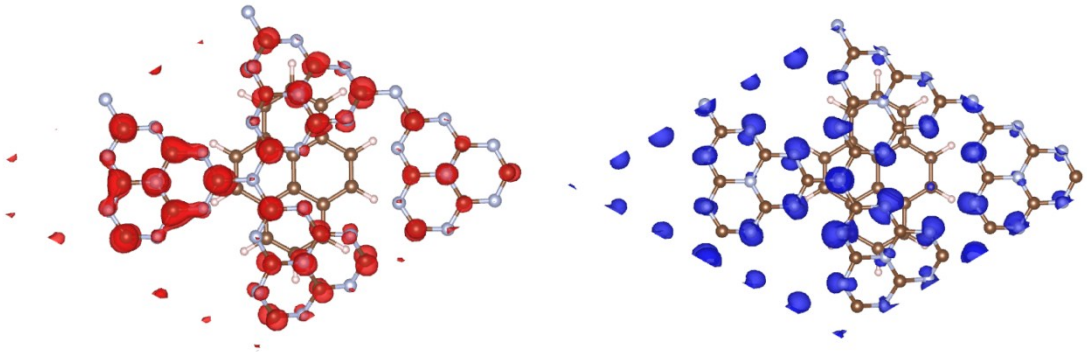

Figure S4. The electron (red) and hole (blue) distribution of the peak *a* in the optical absorption spectrum of C-H/g-$C_3N_4$ shown in Figure 5.

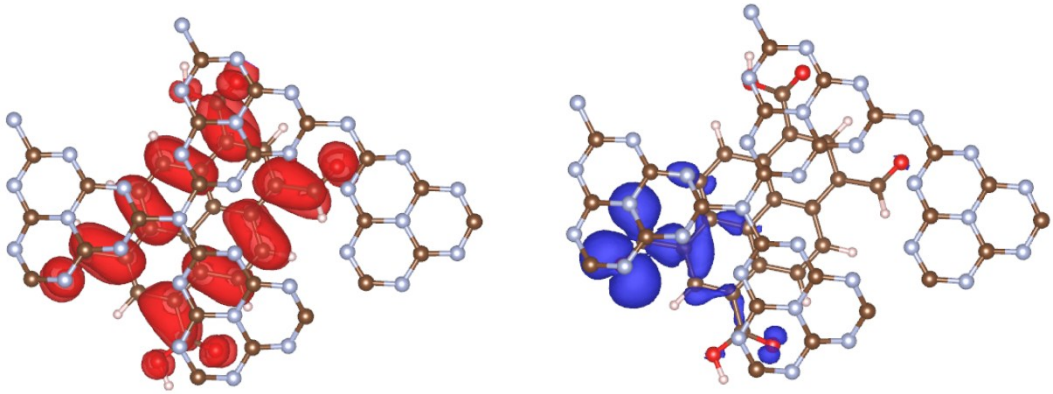

Figure S5. The electron (red) and hole (blue) distribution of the peak *b* in the optical absorption spectrum of C-CHO/g-$C_3N_4$ shown in Figure 5.

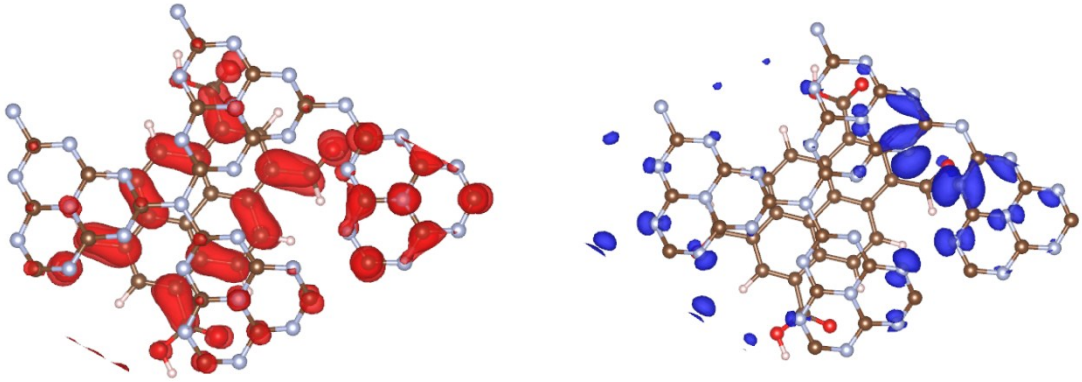

Figure S6. The electron (red) and hole (blue) distribution of the m-CT state in C-CHO/g-$C_3N_4$ which is 0.1 eV above the optical band gap.

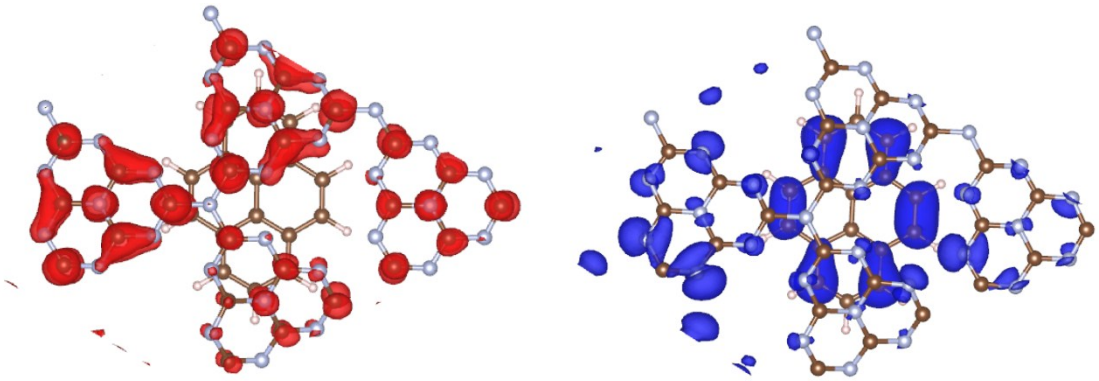

Figure S7. The electron (red) and hole (blue) distribution of the lowest m-CT in C-H/g-$C_3N_4$.

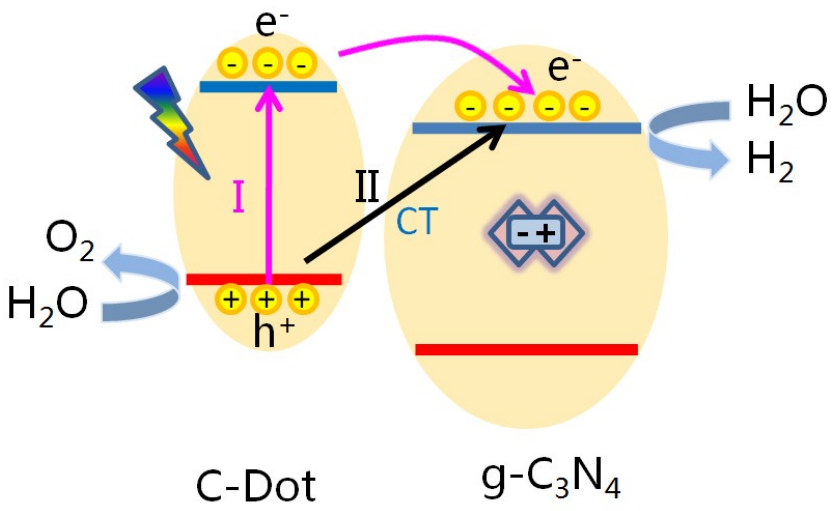


Figure S8. Charge transfer (CT) and separation mechanism in C-H/g-$C_3N_4$ under light irradiation. Route I is a two-step progess. Route II is a direct CT excitation.

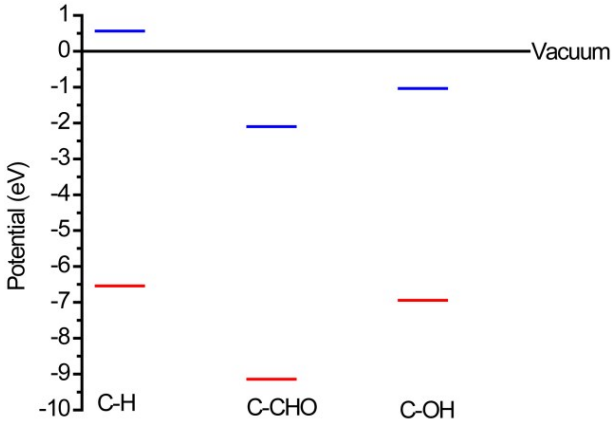


Figure S9. The positions of VBM (red) and CBM (blue) for C-H-Dot, C-CHO-Dot and C-OH-Dot. The vacuum energies of the three kinds of C-Dots are set to zero.

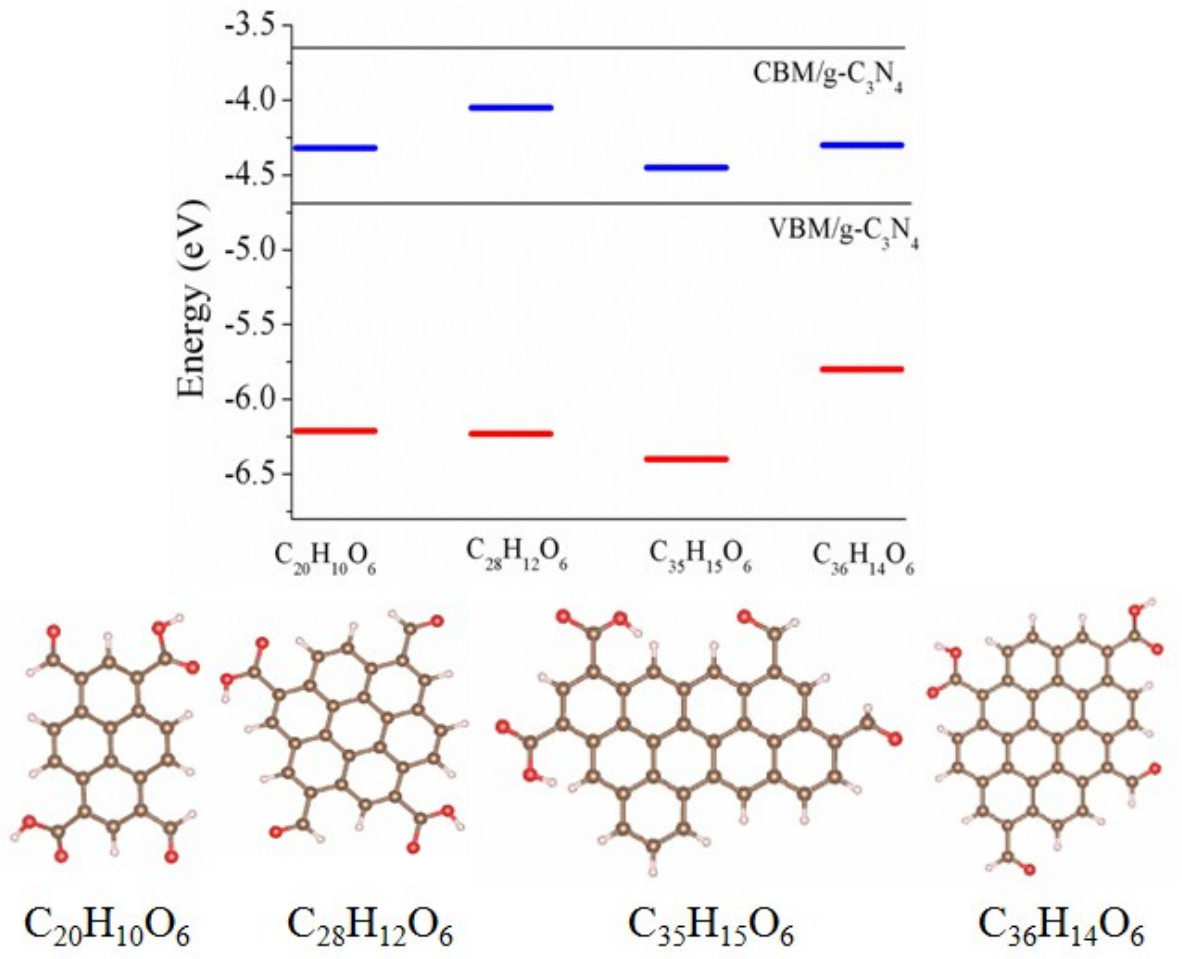


Figure S10. Variation of the DFT HOMO (red) and LUMO (blue) energies of C-CHO-Dot with respect to the vacuum level with the increasing size of the C-CHO-Dot under the condition that the numbers of –COOH and –CHO are kept constant in all the C-CHO-Dot. Position of the VBM and CBM of g-$C_3N_4$ are also indicated.

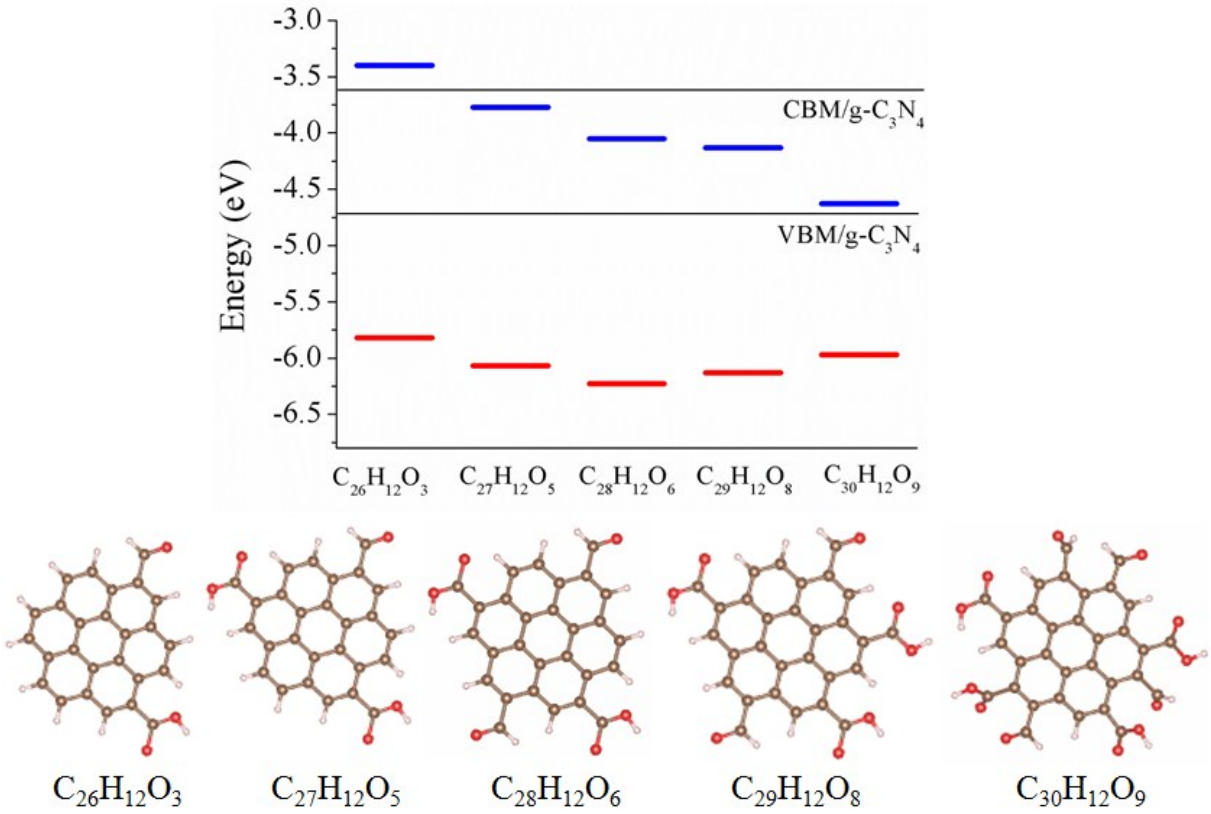


Figure S11. Variation of the DFT HOMO (red) and LUMO (blue) energies of C-CHO-Dot with respect to the vacuum level with the increasing numbers of the –COOH and -CHO under the condition that the size of the C-CHO-Dot is kept constant. Position of the VBM and CBM of g-$C_3N_4$ are also indicated.

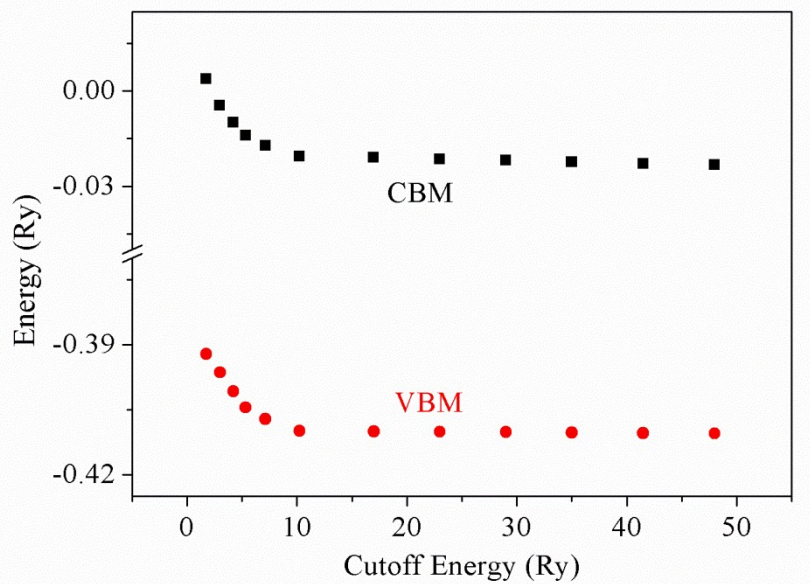


Figure S12. Calculated GW VBM and CBM energies of perfect g-$C_3N_4$ versus cutoff energy of unoccupied orbitals in the screening calculation. The cutoff energy is relative to the CBM energy. All unoccupied orbitals are included in the self-energy calculation. Thickness of vacuum gap in the supercell is 12 Å.

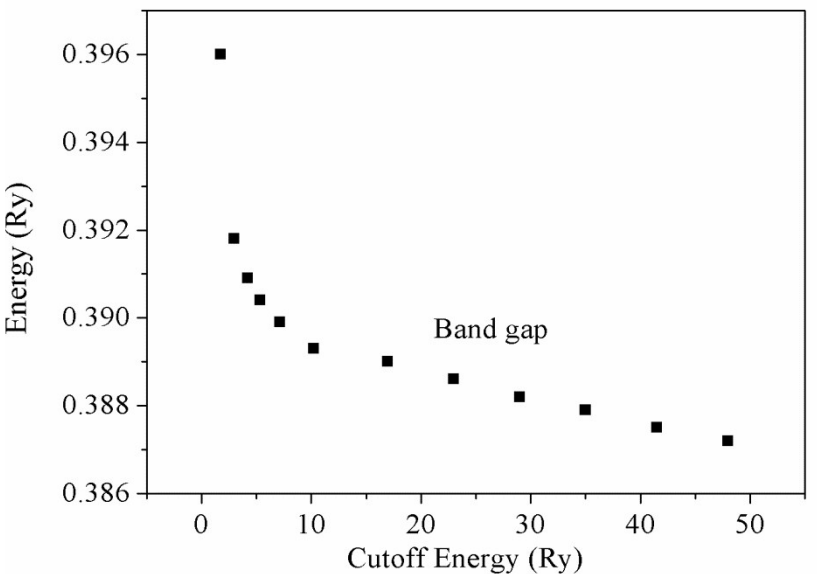


Figure S13. Calculated GW band gap of perfect g-$C_3N_4$ versus cutoff energy of unoccupied orbitals in the screening calculation. The cutoff energy is relative to the CBM energy. All unoccupied orbitals are included in the self-energy calculation. Thickness of vacuum gap in the supercell is 12 Å.

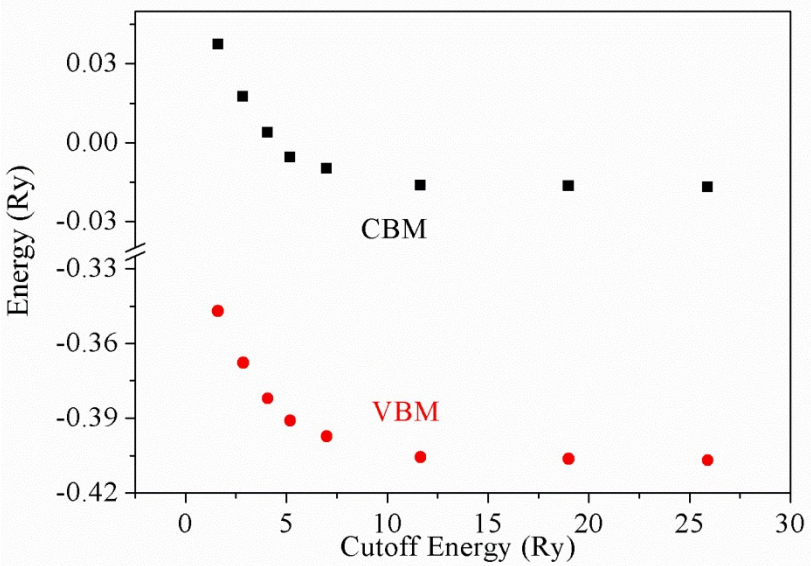


Figure S14. Calculated GW VBM and CBM energies of perfect g-$C_3N_4$ versus cutoff energy of unoccupied orbitals in the self-energy calculation. The cutoff energy is relative to the CBM energy. Unoccupied orbitals with energy smaller than 7.0 Ry with respect to CBM are included in the screening calculation. Thickness of vacuum gap in the supercell is 12 Å.

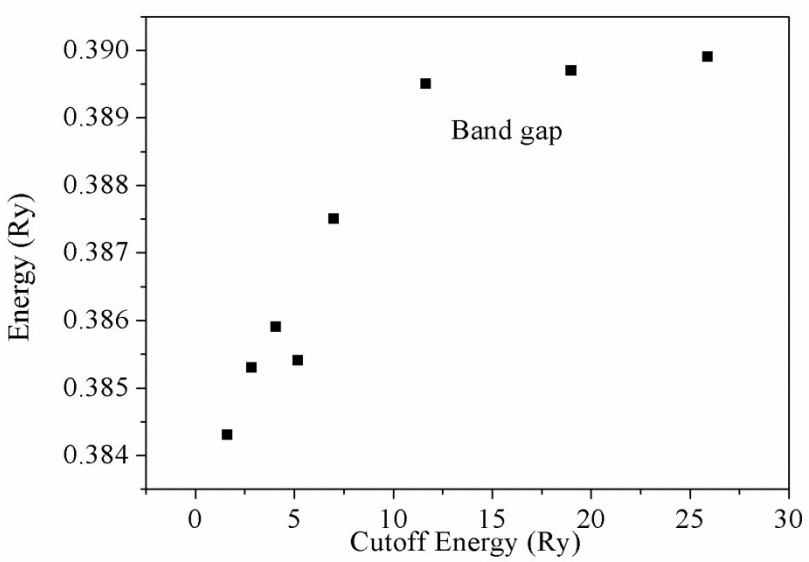


Figure S15. Calculated band gap of perfect g-$C_3N_4$ versus cutoff energy of unoccupied orbitals in the self-energy calculation. The cutoff energy is relative to the CBM energy. Unoccupied orbitals with energy smaller than 7.0 Ry with respect to CBM are included in the screening calculation. Thickness of vacuum gap in the supercell is 12 Å.

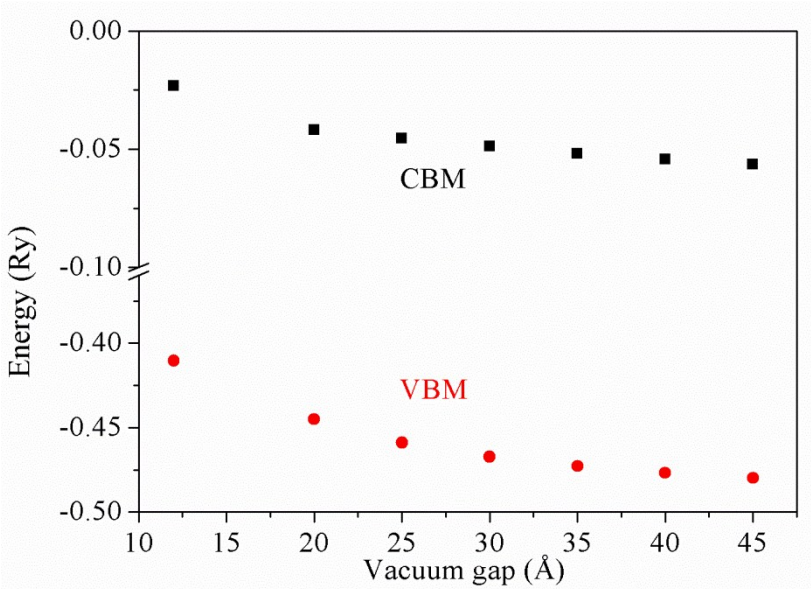


Figure S16. Calculated GW VBM and CBM energies of perfect g-$C_3N_4$ versus the thickness of vacuum gap in the cell. All unoccupied orbitals are included in the band summations in the self-energy and electronic screening calculations.

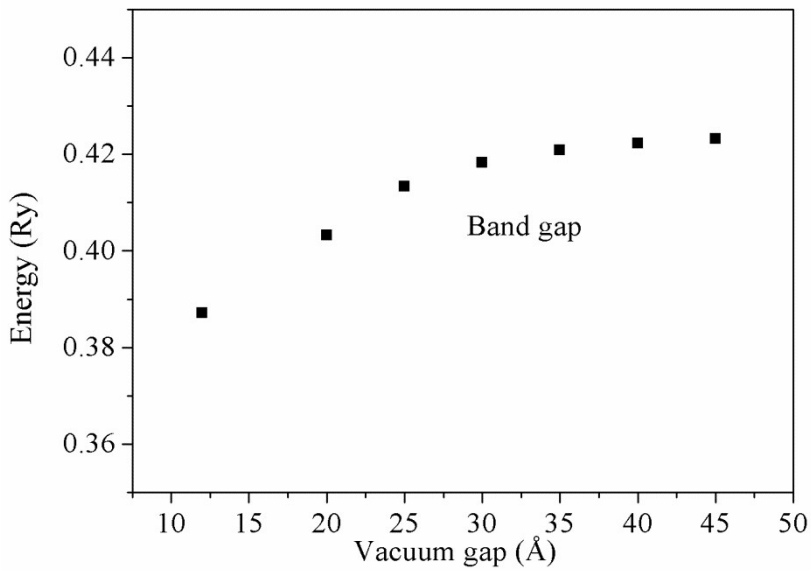


Figure S17. Calculated band gap of perfect g-$C_3N_4$ versus the thickness of vacuum gap in the cell. All unoccupied orbitals are included in the band summations in the self-energy and electronic screening calculations.