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Hybrid DFT Based Prediction of a New Photocatalyst: g-$B_3C_2N_3$

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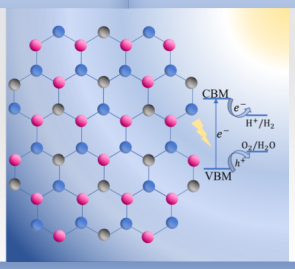
1. Motivation

- Photocatalysis: redox reactions are driven by the energy of the harvested photons.
- Two dimensional (2D) materials offers the advantage of high surface to volume ratio.
- 2D B-C-N systems shows promising prospect as photocatalyst.
- We are proposing a new metal free 2D photocatalyst: g-$B_3C_2N_3$, based on hybrid DFT calculations.



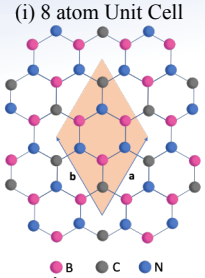
2. Methodology

- Calculations are performed using DFT as implemented in Vienna Ab Initio Simulation Package (VASP)
- Projector augmented method and plane wave basis
- Structural optimization and stability analysis: GGA-PBE functional
- Opto-electronic properties: HSE06 functional

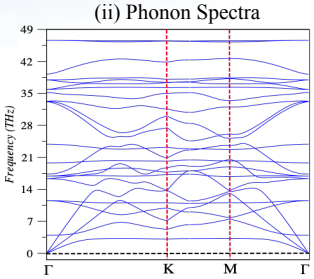
3. Results

(a) Stability of g-$B_3C_2N_3$

(i) 8 atom Unit Cell



(ii) Phonon Spectra



- Formation energy:

$$E_f = E_{B_3C_2N_3} - 3E_B - 2E_C - 3E_N = -9.15 \text{ eV}$$

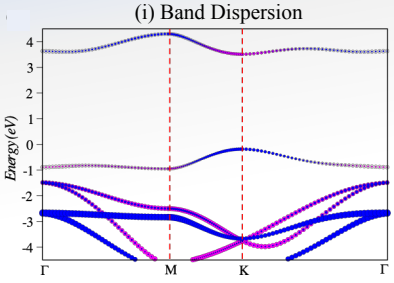
- No imaginary eigen value of dynamical matrix is observed.
- Elastic stability criteria

$$C_{11} = 294.289 > 0$$
$$C_{11} - C_{12} = 294.289 - 58.649 = 235.640 > 0$$

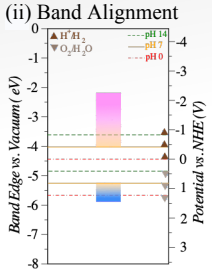
The proposed system is experimentally realizable

(b) Photocatalytic ability

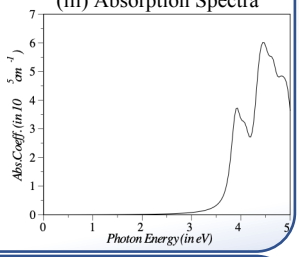
(i) Band Dispersion



(ii) Band Alignment



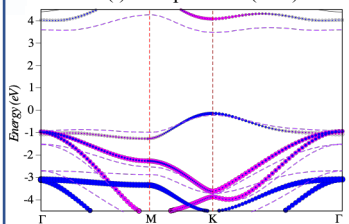
(iii) Absorption Spectra



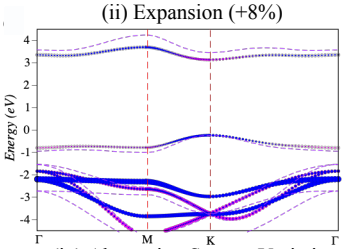
- Direct band gap of 3.69 eV (> 1.23 eV)
- Suitable band edge position over entire pH range
- Harvested photons are in near ultraviolet (UV) range

(c) Effect of Strain on opto-electronic property

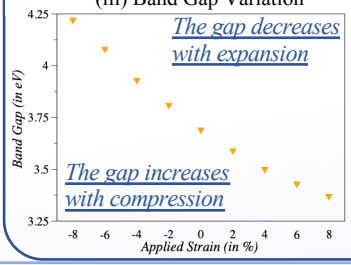
(i) Compression (-8%)



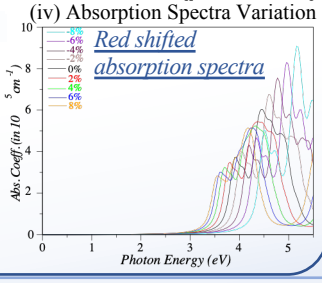
(ii) Expansion (+8%)



(iii) Band Gap Variation

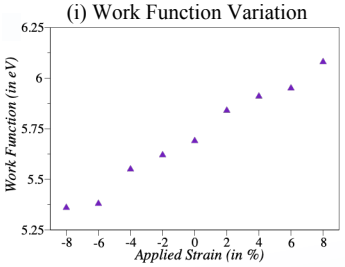


(iv) Absorption Spectra Variation

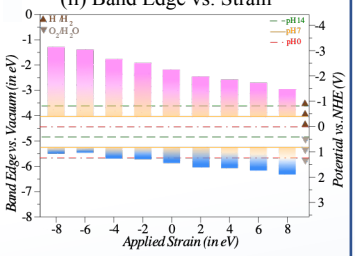


(d) Effect of Strain on photocatalytic ability

(i) Work Function Variation



(ii) Band Edge vs. Strain



- With compression:
  - Reduction offset increases
  - Oxidizing offset decreases
- With expansion:
  - Reduction offset decreases
  - Oxidizing offset increases

Redox offsets can be thoroughly tuned by varying pH and biaxial strain

6. Reference

1. S. Karmakar and S. Dutta, Strain-tuneable photocatalytic ability of BC_6N monolayer: A first principle study. *Comput. Mater. Sci.* **2022**, *202*, 111002
2. S. Karmakar, S. Adhikary and S. Dutta, g-$B_3C_2N_3$: A new potential two dimensional metal-free photocatalyst for overall water splitting. (*Submitted*, **2022**)

7. Acknowledgement

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5. Conclusions

- g-$B_3C_2N_3$ can act as a near UV absorbing green photocatalyst.
- Photocatalytic ability is maintained over entire pH range.
- Tensile strain provides the added advantage of red shifted absorption spectra and balanced HER-OER offsets.
- Precise control over redox reactions is achievable by varying pH and strain.