

Supporting Information

Substitutional Mo Doping in Ta₃N₅ Photoanode: Mitigating Native Defects engineering and Enhancing Water Splitting performance

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DFT Part GGA and GGA+U

In the literature, several methods have been developed to address the limitations of GGA in accurately predicting the bandgap of semiconductors. Approaches such as PBE0, HSE, and GGA+U are commonly employed to approximate bandgaps closer to experimental values. Hybrid functionals like PBE0 and HSE, though effective, are computationally expensive and tend to overestimate bandgap energies [1]. In comparison, the GGA+U method has proven to be a highly efficient alternative [2].

The GGA+U method introduces an on-site Coulomb interaction (U) to selected orbitals, resulting in an upward shift of the conduction band (CB) while leaving the valence band (VB) energies largely unaffected. This shift increases the bandgap, providing a more accurate representation of the electronic structure [3]. For systems like pure and Mo-doped Ta₃N₅, the addition of the Hubbard U parameter enhances the description of electronic properties and aligns computational results more closely with experimental observations [4]. By correcting the GGA method with the Hubbard U parameter, the electronic structure and material properties can be better understood and accurately modeled [5]. The Hubbard parameter, U, is defined as

$$U = uU_{\text{ion}} \quad (1)$$

Here, u is a constant ($0 < U < 10$) determined by calibrating the calculated bandgap to match the experimental bandgap of the system [6], [7]. The U_{ion} values for Ta^{5+} , N^{3-} , and Mo^{4+} are listed in Table S1.

Table S1 U_{ion} values from literature

Ion	U_{ion}	Ref
Ta^{5+}	14.05	[4]
N^{3-}	9.33	[4]
M^{4+}	6.45	[8]

Table S2 u values for present work

u	$U \text{ (eV)} = uU_{\text{ion}}$		
	Ta	N	Mo
0.1	1.41	0.93	0.65
0.2	2.82	1.86	1.29

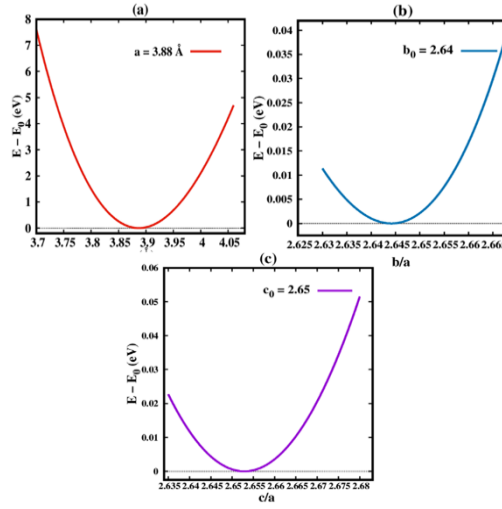


Fig. S1 Theoretical lattice constant (a) b/a ratio and (c) represent the c/a ratio of pure Ta_3N_5 unit cell.

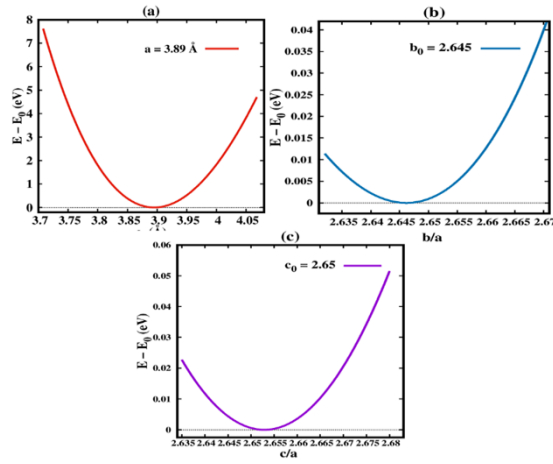


Fig. S2 Theoretical lattice constant (a) b/a ratio and (c) represent the c/a ratio of MTN_x unit cell.

Table S3 Experimental and theoretical lattice parameters of MTN_x.

	A (Å)	B (Å)	C (Å)	α (°)	β (°)	γ (°)	Ref
Experimental	3.88	10.21	10.26	90	90	90	Present Work
Theoretical	3.88	10.24	10.28	90	90	90	Present Work
Theoretical	3.87	10.23	10.29	90	90	90	[9]

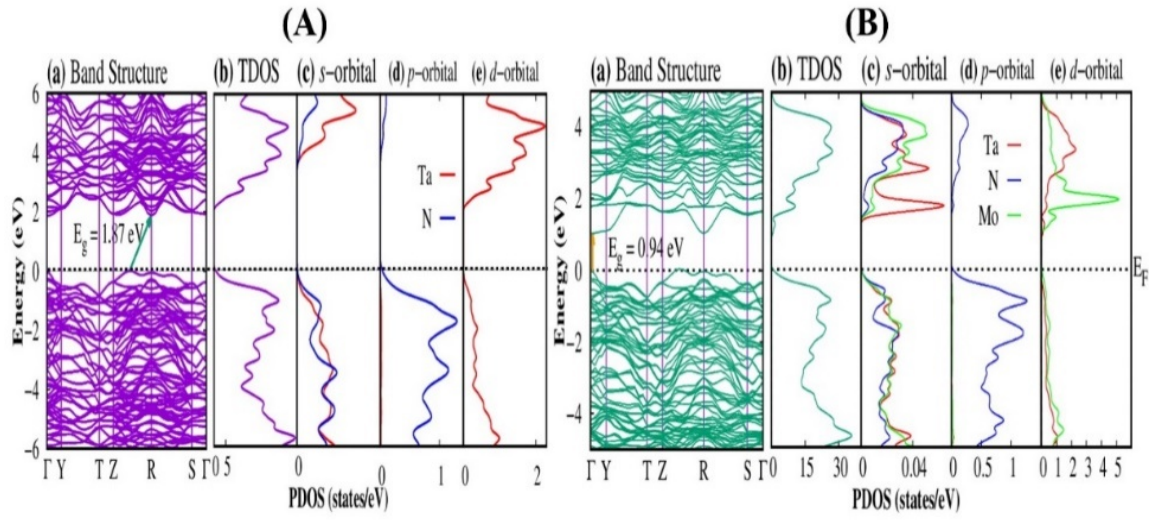


Fig. S3 The GGA+U calculated bandgap for (A) pure and (B) MTN_x where $u = 0.1$.

Table S4 The optical bandgap of bare Ta_3N_5 and MTN_x .

Simple	Optical bandgap with GGA	Optical bandgap with GGA+U	$\epsilon_1^{Average}(0)$ With GGA	$\epsilon_1^{Average}(0)$ With GGA+U
Ta_3N_5	1.40 eV	2 eV	8.9	6
Mo- Ta_3N_5	0.98 eV	1.20 eV	11.58	8.31

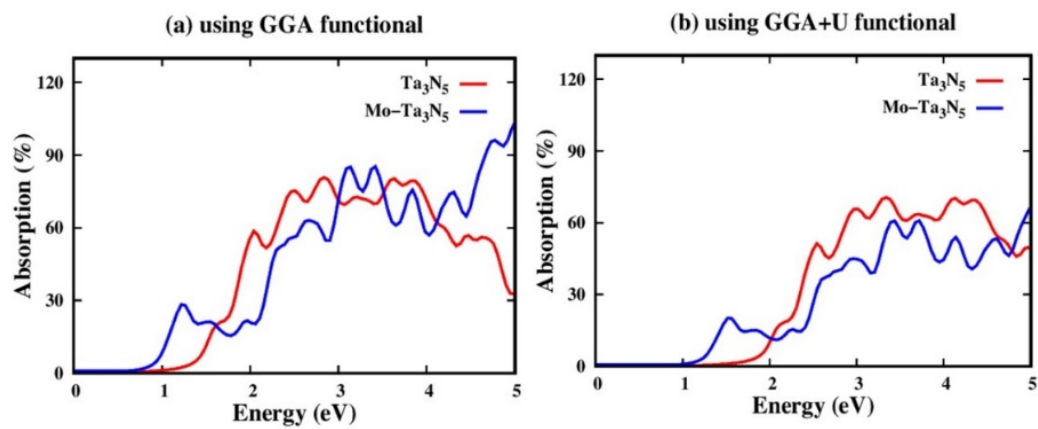


Fig. S4 Absorption coefficient for bare Ta_3N_5 and MTN_x .

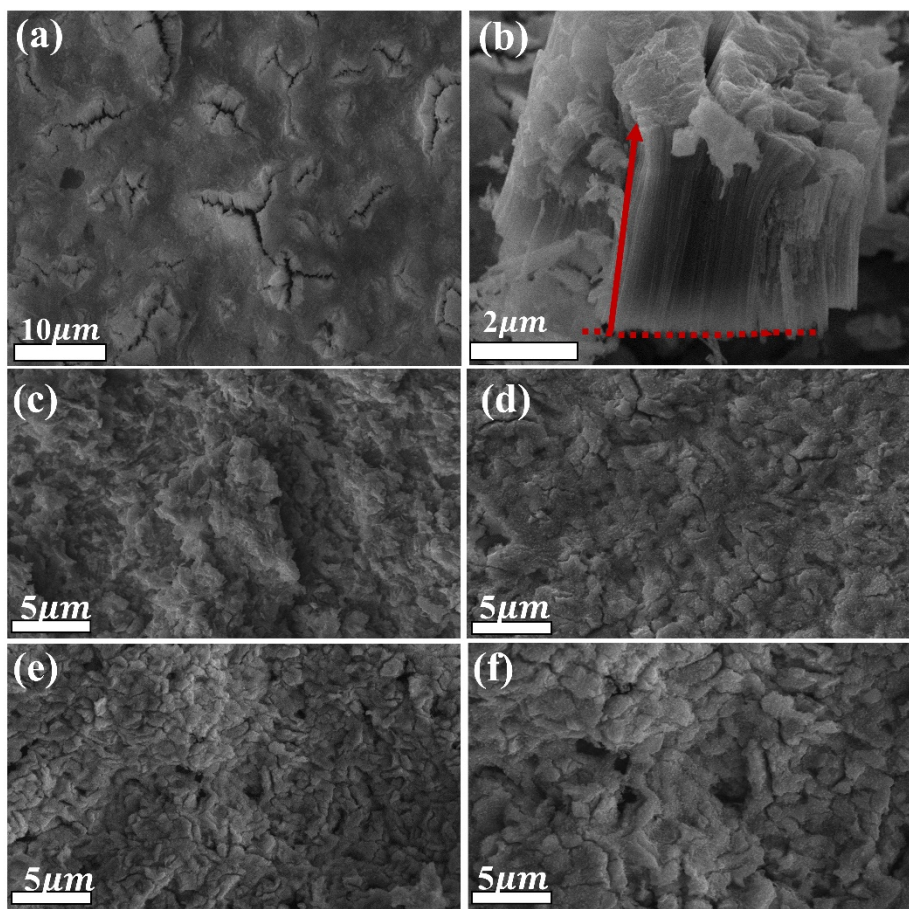


Fig. S5 Top view SEM image of Ta_2O_5 nanotubes (NTs), while (b) is the cross-section view of Ta_2O_5 NTs obtained in the electrolyte containing H_2SO_4 +1Vol% HF + 4 Vol% H_2O . The red arrow represents the length of the NTs while the dash lines highlighted the boundary between Ta substrate and Ta_2O_5 NTs. While (c), (d), (e) and (f) represent the top view of Ta_3N_5 , MTN-0.1, MTN-0.3 and MTN-0.5 respectively.

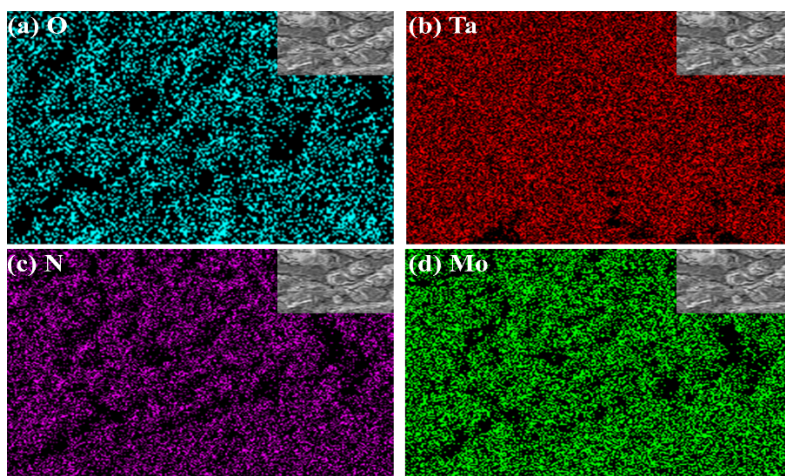


Fig. S6. EDX elemental mapping images of MTN_x .

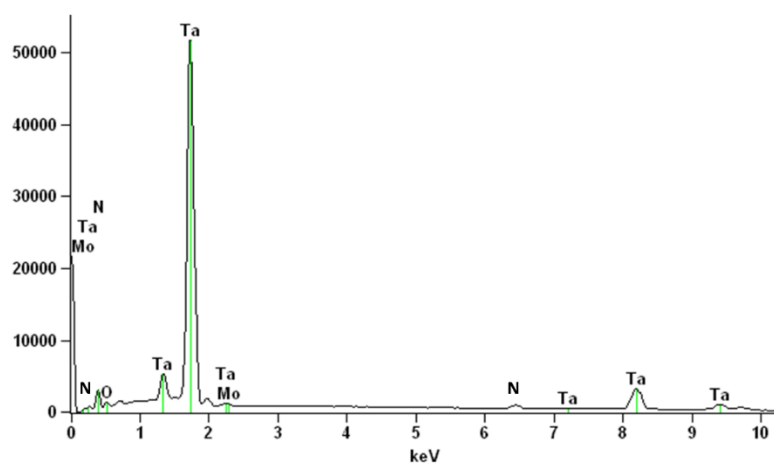


Fig. S7 Energy Dispersive X-ray Spectroscopy (EDX) Elemental Spectrum Analysis of MTN_x .

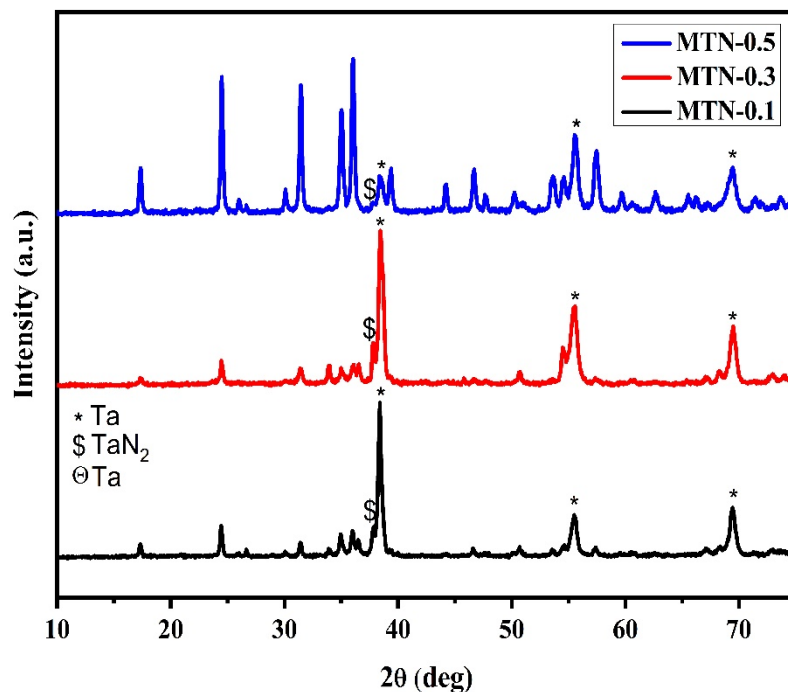


Fig. S8 XRD of Mo doped sample after PEC measurements.

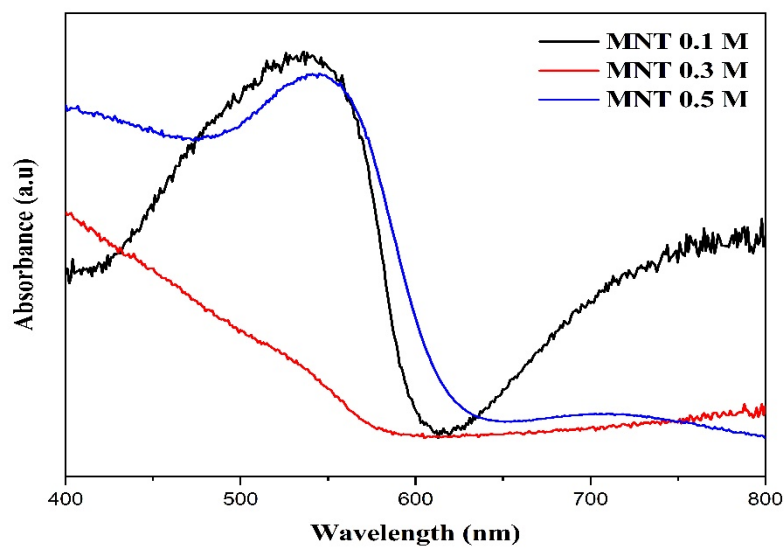


Fig. S9 UV-visible absorption spectra after PEC measurements.

Table S5. EDX table of all samples with wt.% of each element.

Elemental analysis (Wt%)

Sample	O	N	Ta	S	Mo
Ta ₂ O ₅	60.02	0	36.66	3.32	0
Ta ₃ N ₅	5.35	57.44	37.21	0	0
MTN-0.1	6.37	54.99	38.22	0	0.42
MTN-0.3	8	55.60	35.35	0	1.05
MTN-0.5	9	51.68	36.53	0	2.75

Table S6. Experimental bandgap and absorption edge of bare Ta₃N₅ and MTN_x.

Sample	Bang gap (eV)	Absorption edge (nm)
Pure Ta ₃ N ₅	2.10	613
MTN-0.1	2.05	617
MTN-0.3	2.04	640
MTN-0.5	2.05	634

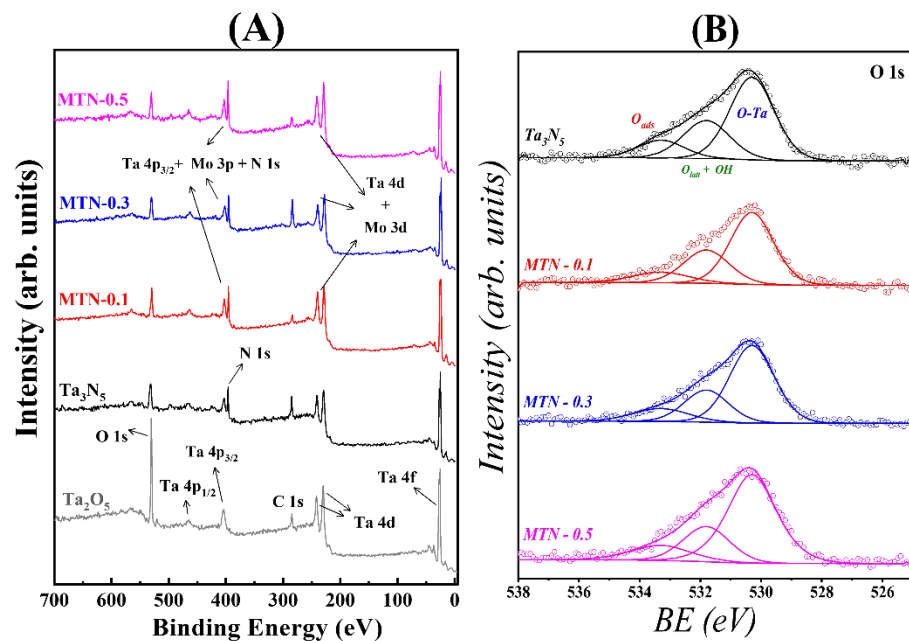


Fig. S10. (a) Survey scan XPS spectra from 0 to 900 eV of bare Ta₃N₅ and MTN_x. (b) Deconvoluted O1s spectra of bare Ta₃N₅ and MTN_x.

Table S7. Summarize results of XPS of bare Ta₃N₅ and MTN_x.

Samples	N/Ta	O/Ta	Mo/Ta	Ref
Ta ₂ O ₅	---	1.70	----	Present Work
Ta ₃ N ₅	1.50	0.20	---	Present Work
Ta ₃ N ₅	1.59	0.22	-----	[79]
MTN-0.1	1.45	0.30	0.10	Present Work
MTN-0.3	1.49	0.50	0.15	Present Work
MTN-0.5	1.58	1.13	0.17	Present Work

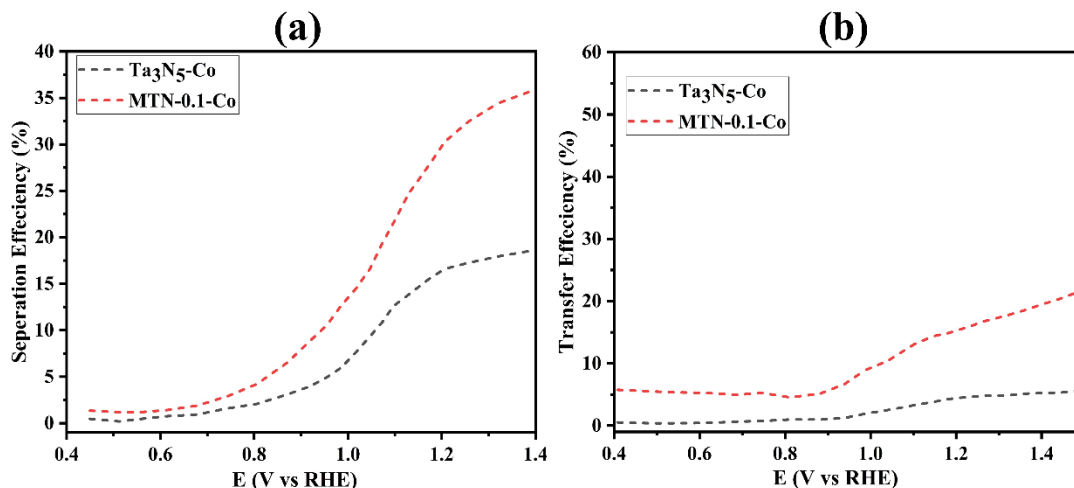


Fig. S11 (a) Bulk charge separation efficiency and (b) surface charge transfer efficiency of bare Ta_3N_5 and MTN-0.1 with $\text{Co}(\text{OH})_x$ co-catalyst.

References

- [1] M. Harb *et al.*, “Tuning the properties of visible-light-responsive tantalum (oxy)nitride photocatalysts by non-stoichiometric compositions: A first-principles viewpoint,” *Phys. Chem. Chem. Phys.*, vol. 16, no. 38, pp. 20548–20560, Sep. 2014, doi: 10.1039/c4cp03594a.
- [2] M. Cococcioni and S. De Gironcoli, “Linear response approach to the calculation of the effective interaction parameters in the LDA+U method,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 71, no. 3, Jan. 2005, doi: 10.1103/PhysRevB.71.035105.
- [3] V. N. Jafarova and G. S. Orudzhev, “Structural and electronic properties of ZnO: A first-principles density-functional theory study within LDA(GGA) and LDA(GGA)+U methods,” *Solid State Commun.*, vol. 325, Feb. 2021, doi: 10.1016/j.ssc.2020.114166.
- [4] H. Jouypazadeh, H. Farrokhpour, and M. M. Momeni, “Theoretical investigation of the water splitting photocatalytic properties of pristine, Nb and V doped, and Nb-V co-doped (1 1 1) TaON nanosheets,” *Appl. Surf. Sci.*, vol. 541, Mar. 2021, doi: 10.1016/j.apsusc.2020.148572.

- [5] J. Wang, T. Fang, L. Zhang, J. Feng, Z. Li, and Z. Zou, "Effects of oxygen doping on optical band gap and band edge positions of Ta₃N₅ photocatalyst: A GGA + U calculation," *J. Catal.*, vol. 309, pp. 291–299, 2014, doi: 10.1016/j.jcat.2013.10.014.
- [6] P. Rani, G. S. Dubey, and V. K. Jindal, "DFT study of optical properties of pure and doped graphene," *Phys. E Low-Dimensional Syst. Nanostructures*, vol. 62, pp. 28–35, 2014, doi: 10.1016/j.physe.2014.04.010.
- [7] P. Krisna Das *et al.*, "Nanoporous Ta₃N₅: Via electrochemical anodization followed by nitridation for solar water oxidation," *Dalt. Trans.*, vol. 49, no. 42, pp. 15023–15033, Nov. 2020, doi: 10.1039/d0dt03056b.
- [8] R. Tesch and P. M. Kowalski, "Hubbard U parameters for transition metals from first principles," *Phys. Rev. B*, vol. 105, no. 19, May 2022, doi: 10.1103/PhysRevB.105.195153.
- [9] H. Jouypazadeh, H. Farrokhpour, and M. M. Momeni, "A DFT study of the water-splitting photocatalytic properties of pristine, Nb-doped, and V-doped Ta₃N₅ monolayer nanosheets," *Surfaces and Interfaces*, vol. 26, Oct. 2021, doi: 10.1016/j.surfin.2021.101379.
- [10] Z. Wang *et al.*, "Insight into the charge transfer in particulate Ta₃N₅ photoanode with high photoelectrochemical performance," *Chem. Sci.*, vol. 7, no. 7, pp. 4391–4399, 2016, doi: 10.1039/c6sc00245e.
- [11] J. Feng *et al.*, "Ge-mediated modification in Ta₃N₅ photoelectrodes with enhanced charge transport for solar water splitting," *Chem. - A Eur. J.*, vol. 20, no. 49, pp. 16384–16390, 2014, doi: 10.1002/chem.201402760.