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Supporting Information

Nanostructured N-doped orthorhombic Nb_2O_5 as an efficient stable photocatalyst for hydrogen generation under visible light

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Fig. S1

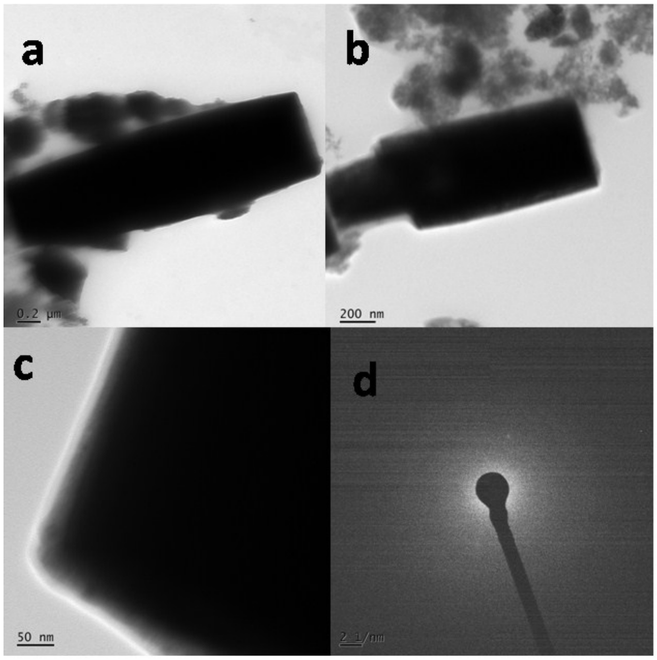

Fig. S1TEM images of nitrogen doped Nb_2O_5 (N-NbO-15) (a-c) low resolution TEM image of N-NbO-15, d) SAED pattern of N-NbO-15

Fig. S2

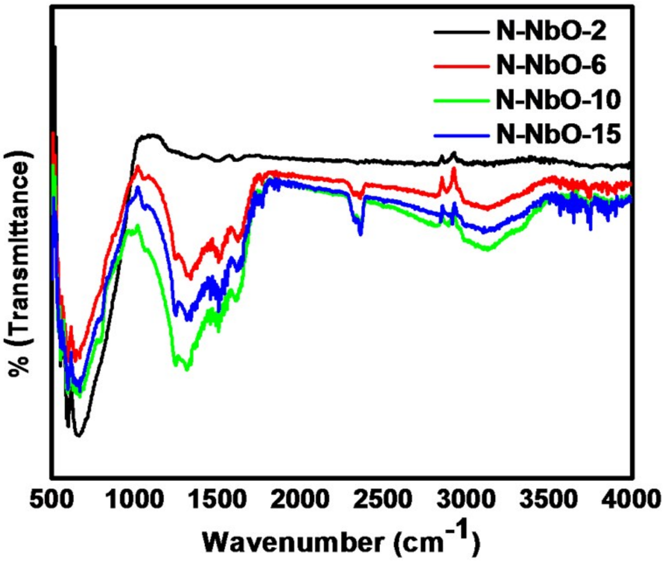

Fig.S2 FTIR Spectrum of nitrogen doped Nb_2O_5 (a) N-NbO-2(Black) (b) N-NbO-6 (Red)(C) N-NbO-10 (Blue)d) N-NbO-15 (Green)

Periodic DFT calculations were carried out with Vienna *Ab Initio* Simulation Package (VASP) code[1-3**]** and the projector augmented wave (PAW) method,[4**]** for which interactions between valence electrons and ion cores are described by pseudopotentials (PP) and the electronic wavefunctions are expanded in terms of a discrete plane-wave basis set up to a plane wave energy cutoff of 520eV. The PAW atomic reference configurations for the Nb, O, and N are $4p^6 4d^4 5s^1$, $2s^2 2p^4$, and $2s^2 2p^3$ respectively. Electron exchange-correlation was treated with the PBEsol parameterization of the generalized gradient approximation (GGA) within Perdew-Burke-Ernzerhof (PBE) functional[5,6**]** Spin polarization has been employed in all calculations.Brillouin zone (BZ) was sampled with a gamma centered 6×6×8Monkhorst-Pack grid**[7]** resulting in100 K- points in the irreducible part of the Brillouine zone with a Gaussian smearing of 0.01 eV. Self-Consistent Field (SCF) calculations of the electronic structure were considered converged if the electronic energy change between two steps was below 10^{-5}. All geometries were optimized using a conjugate gradient algorithm until the forces acting on each atom were converged below 0.01 eVÅ^{-1}.

The $T-Nb_2O_5$ has an orthorhombic crystal structure with partial occupancy. To account for the partial occupancy in theoretical simulations, a minimum of (1×1×5) sized super cell would be needed. This would contain 294 atoms which would require high computational power to perform the electronic structure analysis. In $T-Nb_2O_5$ the oxygen atoms are coordinated to the Nb atom through distorted octahedral/pentagonal bipyramidal structures. To avoid the high computational cost of calculating the electronic structure we have chosena model orthorhombic structure with Nb atoms having octahedral coordination and pentagonal bipyramidal coordination as in the case of $\beta-Ta_2O_5$. This structure represents the typical bonding situation in the orthorhombic $T-Nb_2O_5$. The PBE-sol optimized crystal structure of Nb_2O_5 was taken from literature [8] and re-optimized the coordinates for the pristine and the N-doped case.

The structural model employed for the calculation is given below. Note that the unitcell has multiplied 2 times in all direction for a better visualization. In the pristine Nb_2O_5, the unitcell contains 14 atoms of which 10 are oxygen atoms. In the relaxed structure, the Nb-O bond lengths vary from 1.89 to 2.04 Å in the octahedral coordination and from 2.1 to 2.69 Å in the pentagonal bipyramidal coordination. The closest Nb-Nb distance is 3.38 Å. For the N dopoing one O atom was replaced by a N atom resulting in 10% doping. The configuration yield minimum energy when N is substituted in the xy plane. When N is incorporated, the Nb-O bond length varies from

1.89 to 2.09 Å for the octahedral coordination and from 2.10 to 2.80 Å in the pentagonal bipyramidal coordination. The Nb–N distance is calculated to be 2.28 Å, and the minimum Nb-Nb distance is 3.35 Å.

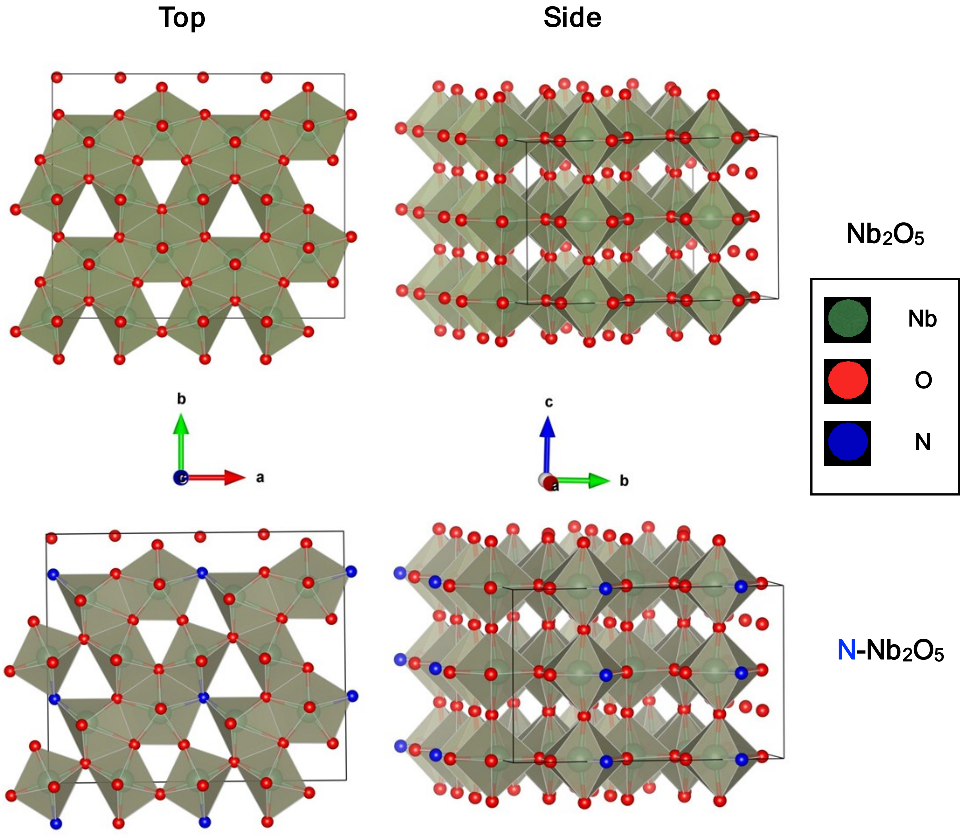

Fig S3: Structural model employed in the present study. The unitcell has repeated twice in all three directions for a better visualization. Top and side view of the pristine Nb_2O_5 is give in the top panel whereas the N doped Nb_2O_5 is given in the bottom panel. Color coding of the atoms are given as inset.

For a better understanding of the electronic structure, the total and atom projected density of states of the pristine and N–doped Nb_2O_5 have plotted in Fig. S2 and S3.In both the case, the lower valence band lies between -18 to -15 eV, which comes mainly from the O-2*s* states. In the case of N–Nb_2O_5 the N2s states falls nearly 3.5 eV above the lower valence band and is separated from the upper valence band by almost 7 eV. The upper valence band consists of an admixture of Nb–4d bands and O–2p bands where in the O–2p orbitals are dominated.

The width of the valence band is nearly 7eV which is a direct consequence of a high level of mixing between the metal 4d orbital and the O/N 2*p* orbitals. In the pristine case the upper edge of the upper valence band has a stronger oxygen 2p character, while in the lower edge it is has equal contribution from the metal and the O atom. The width of the lower conduction band is more than 8eV and is separated from the valence band by an electronic band gap of 1.2 eV. As is expected for the GGA functionals, the band gap is underestimated. Lower edge of the conduction band is predominantly contributed by the metal 4*d* orbital.

On the other hand, when N is incorporated into the system, the valence band is slightly elapsed and at the top of the band there is a much higher mixing of N and O bands with the metal *d* orbitals which might bring more dispersed bands due to orbital overlap. The conduction band is slightly narrowed. Nevertheless, the lower edge of the conduction band is still majorly contributed by the metal *d* orbital. The band gap for the N–Nb_2O_5 is decreased by 0.45 eV and is now 0.75 eV,which agrees very well with the improved photocatalytic activity of the N doped Nb_2O_5 and the red shift in the visible light absorption.

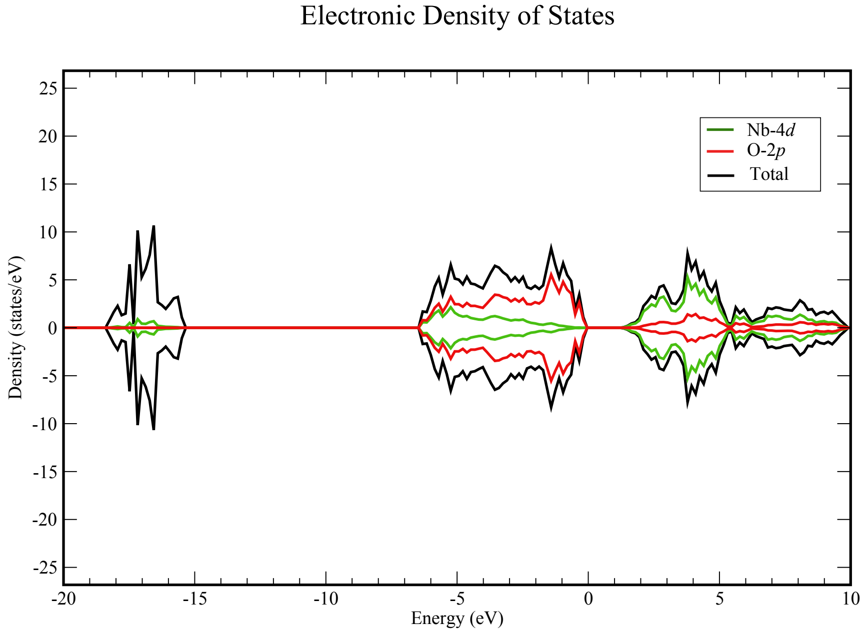

Fig. S4: Total and orbital projected Electronic density of states (DOS) of pristine Nb_2O_5. Black line shows the total DOS while green and red lines showNb–4d and O–2p levels respectively. The Fermi energy is aligned to zero.

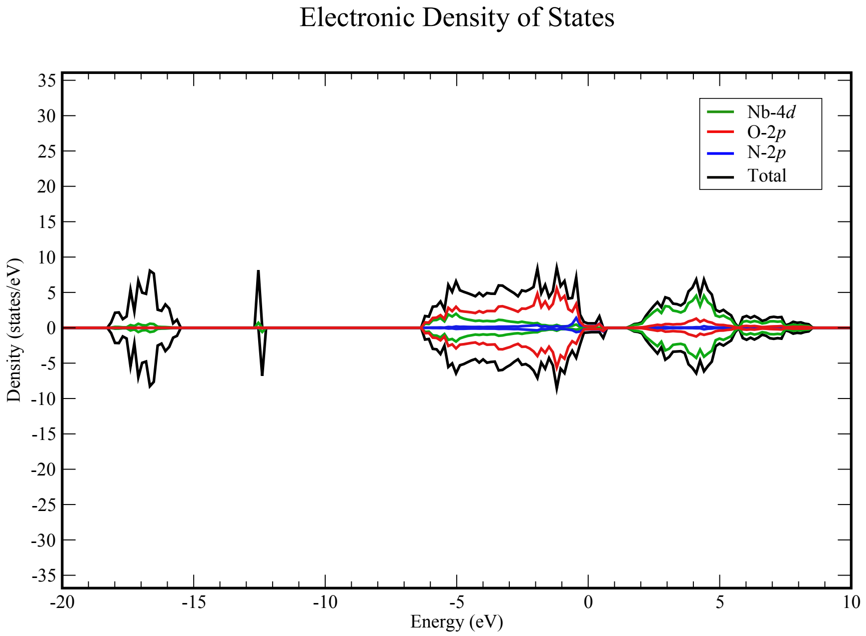

Fig. S5:Total and orbital projected Electronic density of states (DOS) of N doped Nb_2O_5. Black line shows the total DOS while green and red lines showNb–4d and O–2p levels respectively. The blue line represents the 2p orbitals of N. The Fermi energy is aligned to zero.

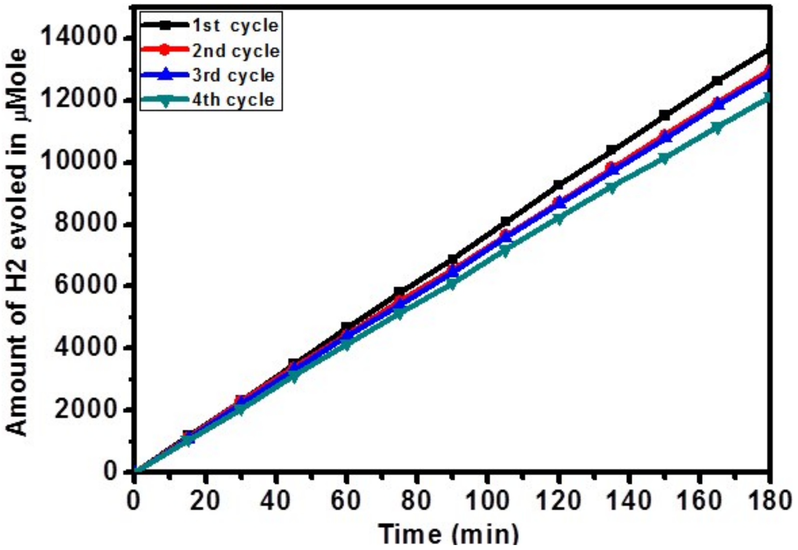

Fig. S6 ::Recycle study of N-Nb_2O_5 (NbO-10) for hydrogen evolution from H_2S

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