Supplementary Material for
"Self energy and excitonic effect in (un)doped TiO_2 anatase : A comparative study of hybrid DFT, GW and BSE to explore optical properties†"

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Validation of functional in context of anisotropy

The nature of anisotropy cannot be determined using only PBE functional. This is clear from (Figure S1) below. Please note that from (Figure S1)(b), S dopants show optically active behaviour in z-direction shown by dotted circle, which is not the case if we use hybrid functional (see Figure 8 in main manuscript). Therefore, it is extremely important to use hybrid DFT or MBPT approach to capture such informations.

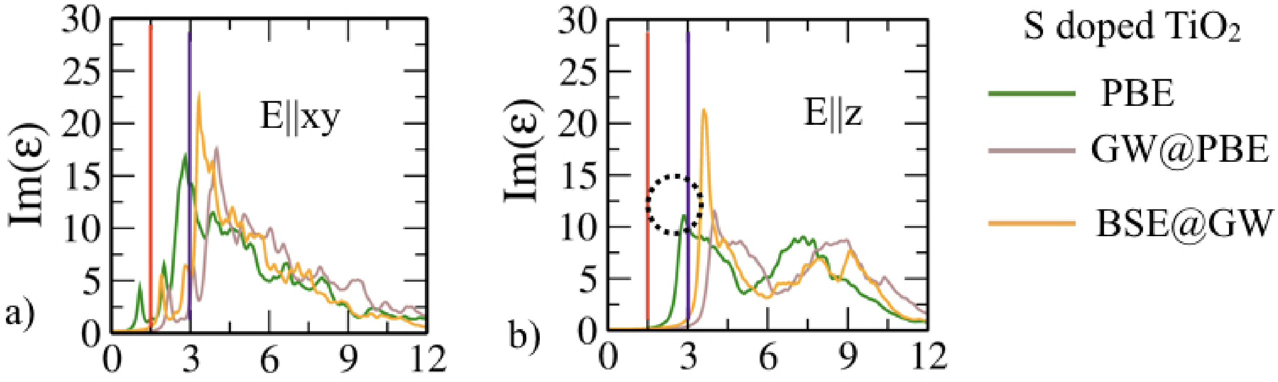

Figure S1: Imaginary part of the dielectric function for S doped TiO_2 using PBE as a starting point (a) E||xy (b) E||z.

Convergence of k-mesh for GW calculations

Kang and Hybertsen obtained a band gap of 3.56 eV [1] using a full-frequency contour-deformation (FF-CD) single shot GW [PBE] approach. Our bandgap value 3.52 eV with k-point 6×6×6 are close in agreement with them as shown in (Figure S2). Therefore, we have used 6×6×6 k-mesh for our quasiparticle calculations.

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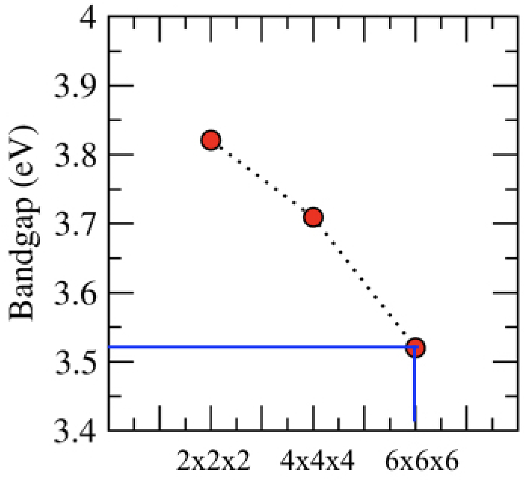

Figure S2: K-point convergence for GW calculations.

Comparison of bandgap obtained from theoretical and experimental results

We have obtained bandgap from substitution of dopant at oxygen site. The theoretical bandgap are compared from literature.

TABLE I: Bandgap obtained from theoretical and experimental results.

Bandgap (eV)	Theoretical (Our work)	Experimental
S_O	2.28	2.29 [2], 2.3 [3]
Se_O	1.89	-
N_O	2.9	2.8 [4]
C_O	2.08	2.0 [5], 2.22 [6], 2.3 [7]

Structure of the charged system

The localised structures of charged systems are very sensitive to the structural distortion due to delocalization of Ti-3d electrons and this will lead to change in bond length for the charged system. Here, we have provided the details of the bond length of the charged system. Note that $\mathrm{S_O}$ and $\mathrm{Se_O}$ are donor type of dopants, whereas $\mathrm{N_O}$ and $\mathrm{C_O}$ are acceptor type of dopants. Hence $\mathrm{S_O}$ and $\mathrm{Se_O}$ prefer positive charge state q = (+1, +2) whereas $\mathrm{N_O}$ will prefer q = -1 and $\mathrm{C_O}$ will prefer charge states q = -1, -2. Therefore we have shown the bond length of the structure with the above mentioned charge states.

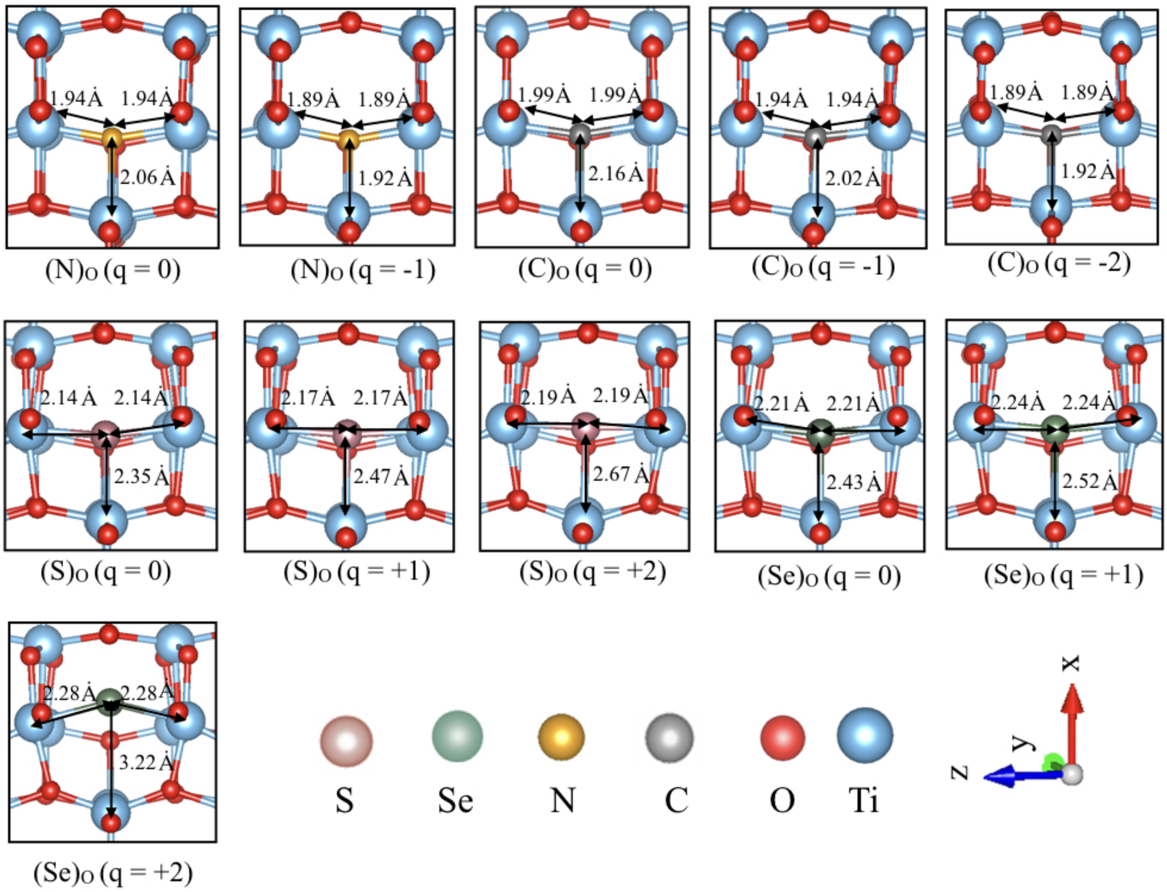

Figure S3: Substitutional defects with various charge states and their bond length.

Interband transitions from density of states (DOS)

We have considered the interband optical transitions throughout our work. GW calculations take care of experimental photoemission and inverse photoemission spectroscopies. It is well known that interband transitions dominate the absorption channel in the mid-/near infrared and visible spectral range. For the N and C-doing case, due to various possible interband transitions as shown by arrow in (Figure S4), we have observed more than one peak below 3 eV (see Figure 10 and 11 in main manuscript).

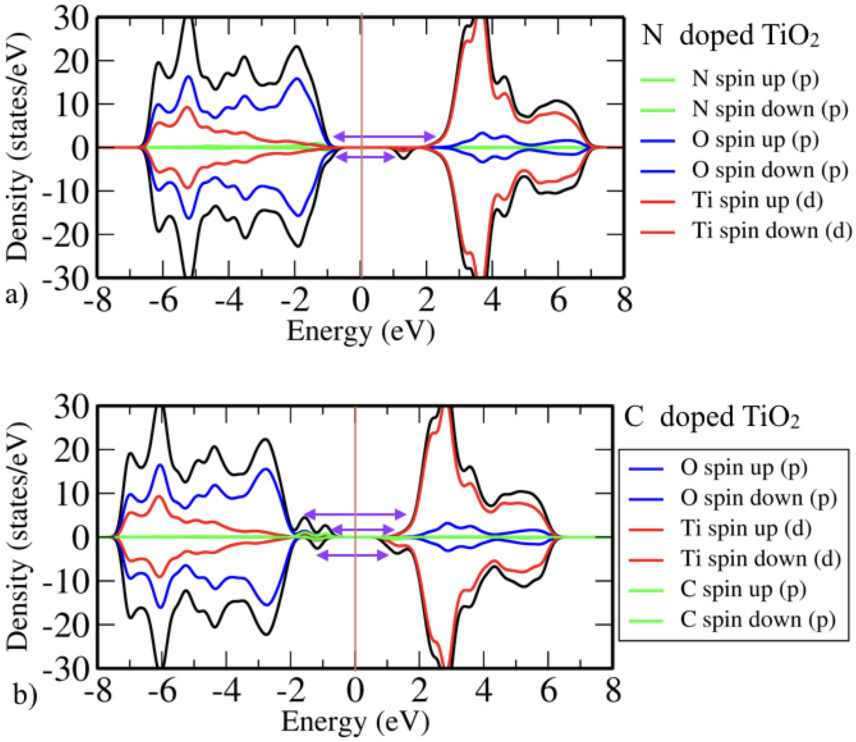

Figure S4: Partial density of states PDOS for (a) N doped TiO_2 (b) C doped TiO_2, where violet arrows show the possible interband transitions.

Starting point for single shot GW calculations

In the (Figure S5), we have used PBE functional as a starting point for the GW calculations. We have also found that GW on the top of PBE or HSE06 give almost similar results for the pristine TiO_2. However, it is well known that PBE is not able to predict accurate position of the defect levels shown by dotted circle in Figure S5(a). Therefore, to have the precise results even with DFT, we have used hybrid functional as a starting point. In the literature, [8] they have also shown that the selection of the functional is not crucial to carry out the GW calculations for the defect-free TiO_2 bulk since both wave functions are very similar. Henceforth all the GW results shown in their work will have as starting point the PBE wave functions. However, the problem of initial wave functions and d-electrons localization description is crucial for defective systems. One cannot exclude a major role of exchange-correlation on starting wave functions, and therefore on electronic-optical properties, when defective systems are considered. In view of this, for TiO_2 anatase one can safely use GW@PBE as in the mentioned literature [9]. However, our primary concern is doped system, where we should be very much careful about the starting point before doing single shot GW calculations. The single shot GW highly depends on the starting point i.e be it with HSE06 or PBE. We find that these are different for various doped systems respectively. Due to unavailability of experimental values, we have no choice but to depend more on advanced functional as starting point rather than doing the same on top of PBE.

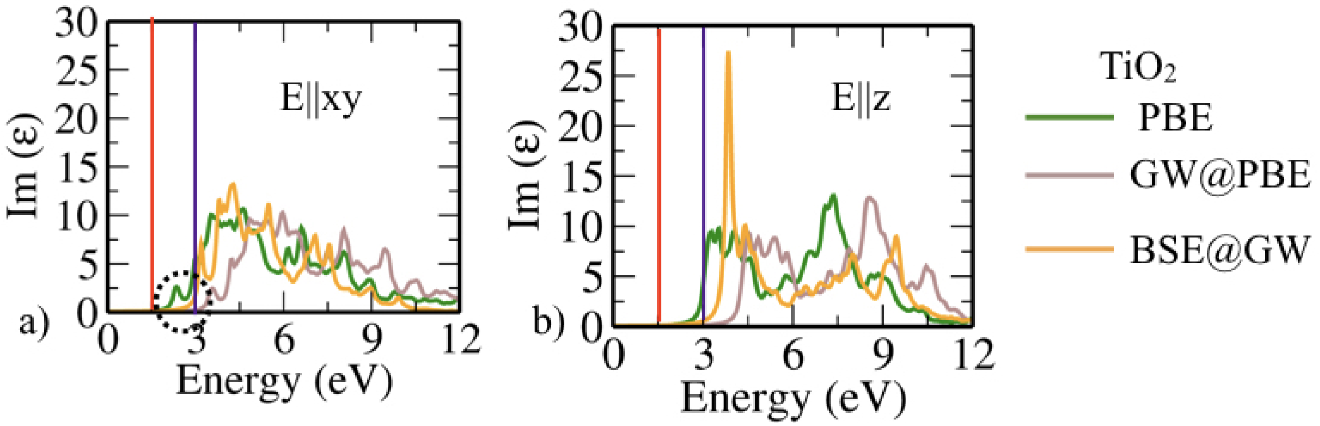

Figure S5: Imaginary part of the dielectric function using PBE as a starting point along (a) E||xy (b) E||z .

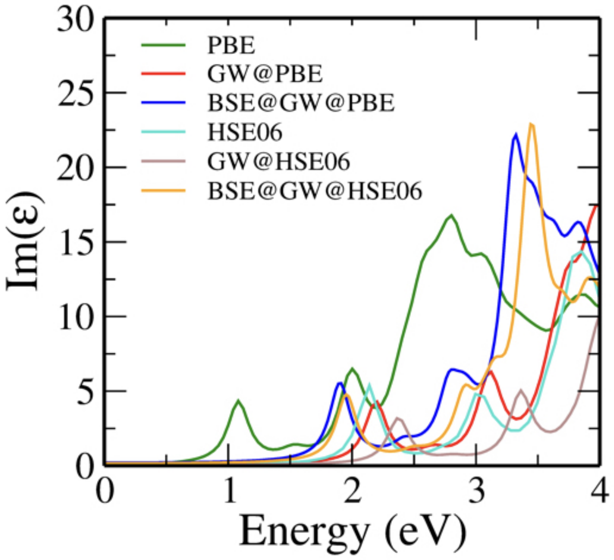

Figure S6: Imaginary part of the dielectric function using DFT and MBPT approaches for S doped TiO_2.

The absorption spectra for the S doped TiO_2 is shown in (Figure S6). We can clearly visualise, the slight difference in absorption peak and edges (see Figure S6). GW@PBE peak position lies at 2.2 eV, whereas peak position obtained from GW@HSE06 at 2.4 eV. The peak position obtained from BSE@GW@PBE = 1.90 eV, whereas BSE@GW@HSE06 = 1.96 eV. There is a slight difference of (0.06 - 0.2 eV). In order to calculate precise position of absorption peaks, it is suggested to use HSE06 as a starting point especially for the doped systems.

Formation energy of transition states

The thermodynamic transition level $\epsilon(q_1/q_2)$ is defined as the Fermi level position for which the formation energies of charge state q_1 and q_2 are equal [10, 11]. The physical significance of this transition level is that for Fermi level below $\epsilon(q_1/q_2)$, charge state q_1 is stable, whereas for Fermi-level positions above $\epsilon(q_1/q_2)$, charge state q_2 is stable. The detailed methodology for the formation energy calculations of X dopants and their stability are given in our previous work [12].

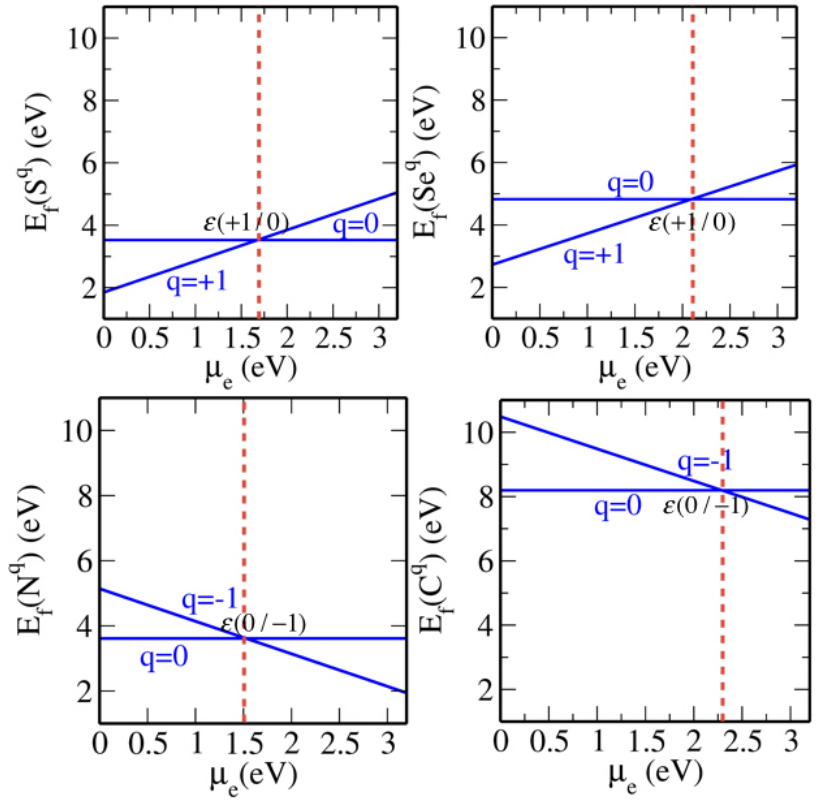

Figure S7: Formation energy of transition states $\epsilon(q_1/q_2)$ for X = S, Se, N and C doped TiO_2.

The thermodynamic transition levels for X dopants are shown below in the table:

TABLE II: Thermodynamic transition levels $\epsilon(q_1/q_2)$ for X dopants.

Dopants	μ_e corresponding to thermodynamic transition levels $\epsilon(q_1/q_2)$
S_O	1.68
Se_O	2.12
N_O	1.50
C_O	2.28

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