

### Research Article

# Strongly Bound Frenkel Excitons on TiO<sub>2</sub> Nanoparticles: An Evolutionary and DFT Approach

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An evolutionary algorithm was employed to locate the global minimum of  $(\text{TiO}_2)_n$  nanoparticles with n = 2 - 20. More than 61,000 structures were calculated with a semiempirical method and reoptimized using density functional theory. The exciton binding energy of TiO<sub>2</sub> nanoparticles was determined through the fundamental and optical band gap. Frenkel exciton energy scales as  $E_B$  (eV) =  $8.07/n^{0.85}$ , resulting in strongly bound excitons of 0.132–1.2 eV for about 1.4 nm nanoparticles. Although the exciton energy decreases with the system size, these tightly bound Frenkel excitons inhibit the separation of photogenerated charge carriers, making their application in photocatalysis and photovoltaic devices difficult, and imposing a minimum particle size. In contrast, the exciton binding energy of rutile is 4 meV, where the Wannier exciton energy scales as  $E_B$  (eV) =  $13.61 \, \mu/\epsilon^2$ . Moreover, the Wannier excitons in bulk TiO<sub>2</sub> are delocalized according to the Bohr radii: 3.9 nm for anatase and 7.7 nm for rutile.

#### 1. Introduction

Titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) are attractive for photocatalytic applications because they exhibit high reactivity related to their high surface area and the unsaturated bonds on the exposed atoms. Furthermore, the nanoparticle reactivity depends on the size, shape, adsorbed water, and hydroxyl groups resulting from the method used during the synthesis [1–7].

The band gap energy is one of the most important electronic properties in semiconducting materials and is strongly dependent on particle size. The size reduction of  $\text{TiO}_2$  NPs favors the oxidation of organic compounds (the increase in the specific surface area offers more catalytic sites) [8]. However, it has the disadvantage in that the band gap is widened, requiring more energy to separate the photogenerated electrons and holes. The quantum confinement effect in the smallest  $\text{TiO}_2$  particles increases the band gap and the exciton binding energy ( $E_{\text{B}}$ ); i.e., the smaller the

 $\text{TiO}_2$  particle, the higher the  $E_{\text{B}}$ . In addition, the experimental difficulties in synthesizing nanoparticles smaller than 3.8 nm impose a size threshold; although it is possible to obtain  $\text{TiO}_2$  colloidal particles with average sizes of 2.1 nm [9], the challenge is to avoid particle aggregation in an aqueous solution.

Photon absorption of TiO<sub>2</sub> leads to the formation of a bound electron-hole pair, i.e., an exciton [10]. In inorganic bulk semiconductors, the energy  $E_{\rm B}$  required to dissociate an exciton into free charge carriers, electrons and holes, is of the order of millielectronvolts. For rutile, e.g., this energy is 4 meV [11], while photoluminescence measurements range from 10 to 20 meV [12]. On the other hand, the experimental direct exciton energy reported for anatase is 180 meV [13], and theoretical calculations using the G<sub>0</sub>W<sub>0</sub> method resulted in a direct optical gap of  $E_{\rm B} = 180$  meV [14]. Therefore, the small  $E_{\rm B}$  for rutile at room temperature causes optical excitations to lead directly to the formation of free charge carriers; i.e., the optical gap ( $E_{\rm opt}$ ) ~ fundamental

gap  $(E_{\text{fund}})$  [10]. Moreover, the exciton binding energy, dependent on the size and shape of nanoscale systems and molecules, is greatly accentuated [15]. For example, the electron-hole exchange interaction increases 1000-fold in quantum dots (QDs) compared to bulk semiconductors [16]. The increase in  $E_{\text{B}}$  shows an adverse effect for TiO<sub>2</sub> NPs used as a photocatalyst since free carriers are necessary to generate oxidizing species such as OH<sup>•</sup> in treating pollutants [4].

Excitons readily formed by photoexcitation can be dissociated into free carriers and thus play a central role in photovoltaic devices [17]. An example is the organolead halide  $CH_3NH_3PbI_6$  perovskite used in solar cells; it has an exciton binding energy of  $55 \pm 20$  meV [18]. Hence, the ultrafine  $TiO_2$  particles (~3 nm) will be useful in solar cell devices if their exciton binding energy is at least of the order of the perovskite.

From a theoretical point of view, the  $E_{\rm B}$  calculation of TiO<sub>2</sub> NPs implies knowing the most stable structures for each nanoparticle size. The search for the global minimum is challenging because of the complexity of the potential energy hypersurface and because the computational resources grow exponentially with the number of atoms in the system. Furthermore, there is no guarantee of finding it. In literature, for example, there are  $(TiO_2)_n$  cluster studies, generally for small systems (n < 20), using density functional theory (DFT) [19–22], hybrid DFT [23–30], GW approach [19, 31–33], time-dependent density functional theory (TDDFT) [19, 24, 25, 34–37], coupled-cluster theory [20, 29, 31], hybrid algorithms [38], and genetic algorithms [39, 40].

The energy difference between the fundamental and the optical gap allows the calculation of the exciton binding energy; however, the calculation of these two properties from theoretical methods needs to be revised. Conventional DFT methods typically underestimated the fundamental gap of insulators and semiconductors by 40% due to the derivative discontinuity of the exact exchange-correlation energy [41]. For instance, an underestimation of around 28% for anatase  $TiO_2$  is reported using the generalized gradient approximation (GGA) exchange-correlation functionals [42, 43].

The optical gap calculation requires the energy of the first excited state, where the TDDFT approach represents the most computationally efficient alternative concerning GW. However, the TDDFT with GGA exchange-correlation functionals systematically underestimates Rydberg and longrange charge-transfer excitation energies by large margins [44, 45]. Hybrid functionals matched with TDDFT typically accomplish better but are often not satisfactory. Turkowski et al. have shown that the TDDFT method can be used to obtain the exciton binding energy for semiconductors [46].

This work presents a comprehensive theoretical methodology to calculate the exciton binding energy of  $(\text{TiO}_2)_n$  NPs with  $n \le 20$ . Since  $E_B$  depends on the size and shape of the cluster, we emphasize the search for the global minimum using an evolutionary algorithm to direct the exploration of stable structures.

The article is structured as follows. Section 2 describes the methodology adopted, introducing the operation of the evolutionary algorithm, the computational details, and the calculation of the exciton binding energy. The results are presented in Section 3 and divided into four subsections. Finally, conclusions are given in Section 4.

#### 2. Methodology

The methodology to compute the exciton binding energy of  $(\text{TiO}_2)_n$  NPs ( $n \le 20$ ) was divided into four stages, shown in the workflow in Figure 1. A detailed description of each stage is presented in the following subsections.

2.1. The Global Minimum Search with an Evolutionary Algorithm. The global minimum search was performed with the USPEX code (Universal Structure Predictor: Evolutionary Xtallography), an evolutionary algorithm developed by Oganov et al. [47-50]. The USPEX program directs the search of the most stable structures by establishing the total energy as a selection criterion. Therefore, an external program must calculate the total energy and perform geometrical optimization. The largest  $(TiO_2)_{20}$  nanoparticle, consisting of 60 atoms, poses a significant computational challenge under the DFT approach for optimizing thousands of structures. For example, USPEX suggested 3184 different structures for 20-unit TiO<sub>2</sub> clusters, as shown in Table S1. This volume of structures to optimize increases the computational cost considerably, making it prohibitive in the context of DFT. Thus, we use the MOPAC program [51] as a geometrical optimizer with the semiempirical Hamiltonian PM6 [52]; the calculations are straightforward, and some 61,000 structures were optimized for all  $(TiO_2)_n$  NPs.

The global minimum search involved calculations over 100 generations, each with a population of 30 structures, except in the first generation, where 40 randomly proposed geometries share the restriction of belonging to one symmetry point group. USPEX implements several variance operators to probe the potential energy surface and thus avoid getting trapped in a local minimum [53, 54]. The populations for the subsequent generations used the following variation operators: 40% heredity, 30% mutation, and 20% permutation of the previous generations; the remaining 10% were random structures. The random structures have a minimum ion distance constraint, avoiding initial structures without any physical meaning; that is,  $Ti - Ti \ge 1.77$ Å, Ti – O  $\ge$  1.173 Å, and O – O  $\ge$  0.726 Å. These values correspond to 60% of the bond length of Ti-Ti in a hexagonal close-packed structure [55], anatase Ti-O [56], and O=O [57], respectively. The geometry optimization comprises three steps, making the convergence criteria more demanding in each progressive step using the MOPAC program. In addition, the final optimization employs a PM6-D3 method, which includes the D3 dispersion correction proposed by Grimme et al. [58].

The evolutionary algorithm is used as a generator of stable structures, at least at the level of the PM6 method. Nevertheless, these structures are only candidates for optimization using density functional theory in the proposed methodology.



FIGURE 1: Workflow to search the global minimum of  $(TiO_2)_n$  clusters. The procedure is applied to each cluster size with  $n \le 20$ , and the energy window is  $\Delta E \le 1.0$  eV.

2.2. Geometry Optimization at the PBE/PAW Level of Theory. The most stable structures from the evolutionary algorithm were considered candidates for relaxing using the VASP5.4.1 code [59], which implements the DFT methodology [60, 61]. The Perdew-Burke-Ernzerhof (PBE) functional [62] was used to include the exchange-correlation energy. The choice of the standard PBE functional can influence the results, mainly when dealing with energetically degenerate structures. We also considered the most stable structures from USPEX within a 1 eV energy window for DFT optimizations to mitigate this effect, as shown in Figure 1. Because the clusters studied were small, with a maximum of approximately 1.4 nm, we did not use the PBEsol functional specifically designed to improve the description of solid systems. The valence electrons of Ti  $(3s^23p^63d^24s^2)$  and O  $(2s^22p^4)$  were expanded on a set of plane waves with a kinetic energy cutoff of 400 eV, whereas the core electrons were described with the projector augmented wave (PAW) approach [63, 64]. The truncation criteria for electronic and ionic loops were set to 10<sup>-4</sup> eV and 10<sup>-2</sup> eV/Å, respectively. In the VASP simulations, the electronic structure of the nanoparticles was determined using single gamma point sampling in the first Brillouin zone. Although nanoparticles exhibit point symmetry, they lack translational symmetry. Finally, all calculations considered spin polarization.

2.3. Exciton Binding Energy of  $TiO_2$  NPs. The structures obtained with the PBE functional were employed as starting geometries for a final geometry optimization using the ORCA4.0.1 code [65] and the hybrid PBE0 functional [66], which takes into account 25% of the Hartree-Fock exact cor-

relation energy. These calculations include the D3 dispersion correction. Effective core potentials (ECP) were used to describe Ti and O core electrons in ORCA calculations [67, 68]. The valence electrons of Ti  $(3s^23p^63d^24s^2)$  and O  $(2s^22p^4)$  were represented by the def2-TZVP basis set (triple-zeta valence with polarization) [69]. Moreover, the resolution of identity (RI) was used to speed up calculations, approximating ordinary two-electron integrals (RI-J) by linearly combining auxiliary def2/J basis functions [70]. In addition, the RIJCOSX approach was adopted to accelerate the computations with hybrid functionals.

The cation and anion structures were also obtained for each  $(\text{TiO}_2)_n$  NP, taking the neutral optimized nanoparticle (PBE0/def2-TZVP) as the initial structure. Finally, a frequency analysis was performed to verify that the final structures correspond to true minima on the potential energy surface.

The following equations were used to calculate the adiabatic ionization potential (IP, removing an electron from the neutral system) and the adiabatic electron affinity (EA, adding an electron to the neutral species):

$$IP = E[X(N-1)]^{+} - E[X(N)], \qquad (1)$$

$$EA = E[X(N)] - E[X(N+1)]^{-}, \qquad (2)$$

where  $E[X(N-1)]^+$  corresponds to the total energy of the cation ground state with (N-1)-electron, E[X(N)] is the total energy for the neutral *N*-electron ground state, and  $E[X(N+1)]^-$  stands for the energy of an anion (N+1)-electron ground state of  $X = (\text{TiO}_2)_n$  with  $n \le 20$ .

The fundamental gap ( $E_{\text{fund}}$ ) is defined according to the following expression [10, 25, 41]:

$$E_{\rm fund} = \rm IP - \rm EA,$$
 (3)

while the optical gap  $(E_{opt})$  corresponds to the energy of the lowest electronic transition (first excited state optically allowed) accessible via absorption of a single photon. Bredas [10] states that

$$E_{\rm opt} = E[X(S_1)] - E[X(S_0)].$$
 (4)

 $E[X(S_0)]$  denotes the total energy of the ground state with singlet multiplicity, and  $E[X(S_1)]$  is the total energy of the first excited state with singlet multiplicity. The spin must be conserved during the electronic transition to neglect the most complex scenarios where optically forbidden states might occur. Therefore, for each  $(TiO_2)_n$  neutral ground state geometry, the first excited state was calculated using the time-dependent density functional theory (TDDFT) [71, 72] in the Tamm-Dancoff approximation (TDA) [73, 74] implemented in the ORCA program. The exciton binding energy ( $E_B$ ) was computed as follows:

$$E_{\rm B} = E_{\rm fund} - E_{\rm opt}.$$
 (5)

The Ti–O bond length, volume, and coordination number of  $\text{TiO}_2$  NPs were analyzed in the Multiwfn 3.7 program [75]. The XRD pattern and the atomic pair distribution function (PDF) were calculated using the Debyer code [76]. The surface area of the particles was determined using the VEGA program [77].

2.4. Exciton Energy of Anatase and Rutile Using the Wannier Exciton Model. For bulk anatase and rutile, the electron and hole effective masses were determined by fitting the top of the valence band (for the hole,  $m_h^*$ ) or the bottom of the conduction band (for the electron,  $m_e^*$ ) with a parabolic function, as in Ref. [42, 78]. The reduced mass of the exciton ( $\mu$ ), the effective masses of the electron and the hole, and the dielectric constant ( $\varepsilon_r$ ) were computed using the following equations [79]:

$$\frac{1}{m_e^*} = \frac{2}{3m_{e,\perp}^*} + \frac{\varepsilon_{r,\perp}}{3\varepsilon_{r,\parallel} ||m_e^*||},$$
(6)

$$\frac{1}{m_{h}^{*}} = \frac{2}{3m_{h,\perp}^{*}} + \frac{\varepsilon_{r,\perp}}{3\varepsilon_{r,\parallel}m_{h}^{*}\parallel},$$
(7)

$$\varepsilon_r = \sqrt{\varepsilon_{r,\perp}\varepsilon_{r,\parallel}},\tag{8}$$

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}.$$
 (9)

The symbols  $\parallel$  and  $\perp$  refer to the longitudinal and perpendicular axes, [001] and [110] directions, respectively. For anatase,  $[001] = Z - \Gamma$  and  $[110] = \Gamma - X$ , whereas for rutile,  $[001] = Z - \Gamma$  and  $[110] = \Gamma - M$ ; see routes in the 3D Brillouin zone on Figures S7(b) and S8(b).

The band structure calculations were performed in the VASP program using the PBE and PBEsol functionals [80]. The PBEsol exchange-correlation functional was chosen as it has been shown to accurately reproduce the experimental lattice parameters [81]. For recovering the electron correlation effects-at least in pairs-and the Ti 3d orbital additional repulsion, the Hubbard  $U = 5.5 \, \text{eV}$  parameter is applied. This approach has proven to be adequate for studying TiO<sub>2</sub> by our research group [42, 43]. We used the PBE + U methodology instead of a hybrid functional because of the need to calculate the dielectric constant of TiO<sub>2</sub> in volume using the density functional perturbation theory considering the more favorable computational cost of the PBE + U. More details are reported in the third section of the supplementary material (available here). The effective mass of electrons and holes was calculated in the Vaspkit-1.3.1 program [82].

The dielectric constant represents the ability of a dielectric material to screen the external electric field through polarization phenomena. This polarization results from the reorganization of the electronic density or the motion of the ions constituting the material [78]. The dielectric constant induced by the electronic density is named  $\varepsilon_{\infty}$ , and the contribution to the dielectric constant, involving ionic motion, is named  $\varepsilon_{vib}$ :

$$\varepsilon_r = \varepsilon_{\infty} + \varepsilon_{\rm vib}.\tag{10}$$

The dielectric constant  $\varepsilon_r$  can be estimated from the high-frequency dielectric constant  $\varepsilon_{\infty}$ . Since  $\varepsilon_r = \varepsilon_{\infty} + \varepsilon_{\text{vib}}$ , this approximation implies that  $\varepsilon_{\rm vib} = 0$ . The role of ionic motion in influencing the dielectric constant is critical when the movement of ions within the material substantially affects its dielectric properties. This effect is especially pronounced in ferroelectric and piezoelectric materials and those undergoing structural phase transitions. However, in the case of TiO<sub>2</sub>, such phenomena were absent, allowing for the initial neglect of the contribution of the vibrational dielectric constant. Nonetheless, it should be noted that in ionic materials characterized by soft vibrational modes, especially those containing elements with high electronegativity at the top of the periodic table, the vibrational dielectric constant can be notably strong [78]. A different issue is whether to apply the static  $\varepsilon_r$  or high-frequency  $\varepsilon_{\infty}$  dielectric constant in Eq. (11). This question has not yet been clarified so far [83]. The exciton binding energy is calculated by

$$E_{\rm B} = \frac{\mu}{\varepsilon_r^2} E_{\rm Ry},\tag{11}$$

with  $E_{Ry} = 13.61 \text{ eV}$ . This expression is valid when the exciton is delocalized on several unit cells and can be treated as a hydrogen atom (the hole being the proton). This model is called the Wannier exciton [83].

In summary, the global minimum search was conducted with an evolutionary algorithm using semiempirical methods to explore thousands of structures. From the evolutionary algorithm results, the candidate clusters with the lowest energy were reoptimized using the density functional theory within the GGA approach. In the last stage, the ground state of each cluster size was reoptimized using the hybrid PBE0 functional. This process was performed to calculate the total energy and energy of the first excited state using TDDFT. The cluster structure varied slightly depending on the functional used: PBE or PBE0. Finally, the exciton binding energy for the TiO<sub>2</sub> NPs was determined by calculating the fundamental and optical band gap. In contrast, Wannier's exciton model was used to obtain the exciton energy of anatase and rutile.

#### 3. Results

3.1. Performance of the Evolutionary Algorithm. The USPEX program directed the search using an evolutionary algorithm to locate the global minimum of  $(\text{TiO}_2)_n$  NPs, with  $n \le 20$ . A number of 61,128 structures were optimized using the PM6-D3 model implemented in the MOPAC program. Overall, the number of generations required to find the global minimum is less than 100 (the limit of generations used in the search) except for the  $(\text{TiO}_2)_1$  cluster, where 100 generations were needed. The heredity variation operator generated 42% of the global minimums, while the random variation operator produced 32% of the most stable structures; see Table S1. Therefore, proposing structures randomly in each generation is essential to locate the global minimum, even though they only correspond to 10% of the initial structures.

From the results of the PM6-D3 model,  $TiO_2$  NPs stabilize energetically as the systems increase in size, which is related to the saturation of the bonds by decreasing the proportion of surface atoms. The total energy per atom falls with the nanoparticle size, and it converges for the system with n = 20 units of TiO<sub>2</sub> (Figure 2). Accordingly, we analyzed the search for the global minimum for this nanoparticle. Figure 3 shows the rapid improvement of the population quality from the first generations of  $(TiO_2)_{20}$ , although the global minimum was found after evaluating 1590 structures in generation 51 (Table S1). However, USPEX continues to improve the general quality of the population, founding new very-low-energy structures. Similar behavior occurs for smaller TiO<sub>2</sub> NPs.

3.2.  $TiO_2$  NP Ground States. The low-energy structures obtained by the PM6-D3 model from USPEX were considered as initial structures for subsequent optimization with the PBE functional within the GGA approach. Finally, the global minimum obtained with the PBE functional was reoptimized using the PBE0/def2-TZVP level of theory. The structures of the most stable  $(TiO_2)_n$  NPs are shown in Figure 4. The XYZ structures of the TiO<sub>2</sub> NPs are available on GitHub [84].

All nanoparticles have at least one oxygen bound through a single bond. Small particles (n < 13) have two single-bonded oxygens. These oxygens will give rise to hydroxyl –OH in an environment where protons are available; these reactive oxygens can leave the nanoparticle, generating oxygen vacancies which increase the  $E_{\rm B}$  [85]. This study found that particles with n < 9 have symmetry; i.e., (TiO<sub>2</sub>)<sub>8</sub> shows a C<sub>2h</sub> point group, while with n > 9, the nano-

particles are not symmetrical (Table 1). The symmetry arises because USPEX proposes symmetric random structures according to the allowed point groups. Table 1 presents the geometrical parameters of  $TiO_2$  NPs obtained at the PBE0/ def2-TZVP level of theory.

The coordination number (CN) of Ti atoms in bulk anatase and rutile is 6, corresponding to a Ti–O octahedra (CN = 6), and that of O–Ti is 3, as required by stoichiometry. In amorphous TiO<sub>2</sub> NPs, different Ti and O coordination numbers may arise due to both greatly distorted coordination polyhedra and the reduced O–Ti coordination for near-surface O. Table 1 shows the coordination number of Ti–O (Ti CN) and O–Ti (O CN). The Ti CN is in the range of 4.0-4.9, which agrees with the value of 4.8 reported by Chen et al. [87] using an extended X-ray absorption fine structure (EXAFS) for titania particles of 3 nm diameter. Similarly, Yeung et al. [88] reported Ti CN = 4.5 for 3 nm TiO<sub>2</sub> by EXAFS fitting.

The Ti CN for nanoparticles with 18, 19, and 20 units is 4.8, 4.9, and 4.5, respectively, indicating that  $(TiO_2)_{18}$  mainly comprises Ti–O pentahedra (CN = 5). In contrast,  $(TiO_2)_{19}$  is built of TiO<sub>2</sub> octahedra (CN = 6) and pentahedra (CN = 5) (Figure S1). Moreover,  $(TiO_2)_{20}$  mainly presents TiO<sub>2</sub> tetrahedra (CN = 4); see Figures S1 and S2. Our results are in agreement with a study by Fernández-García et al. [89]. They concluded that five coordinated Ti atoms are present in amorphous TiO<sub>2</sub> based in the X-ray-Absorption-Near-Edge Structure (XANES) spectra.

The XRD pattern of the  $(\text{TiO}_2)_{20}$  nanoparticle (Figure S3) shows no strong diffraction peaks. Therefore, the structure is "X-ray amorphous"; i.e., it cannot be identified as an anatase or rutile phase. Similar behavior was found for  $(\text{TiO}_2)_{18}$  and  $(\text{TiO}_2)_{19}$  nanoparticles.

The Ti–O bonds (i.e., 1.857 Å for n = 20) are shorter than those in bulk anatase (four bonds, 1.934 Å; two bonds, 1.980 Å; average, 1.949 Å) [86]. Furthermore, the reduction of the coordination number is due to the atoms at the interface of the nanoparticles. This follows from bond valence analysis; i.e., smaller Ti-O CN is consistent with shorter Ti–O bonds [90]. In previous studies using X-ray spectroscopy [87, 88], researchers generally pointed out the reduction in the Ti coordination number and the shortening of the Ti–O bond in nanometric amorphous titania or very small titania nanoparticles. Yeung et al. [88] showed by EXAFS that the Ti–O bond length is 1.93 Å for a 3 nm TiO<sub>2</sub> sample.

The atomic pair distribution function (PDF) obtained from  $(\text{TiO}_2)_n$  (n = 18, 19, and 20) reflects the atomic correlation in the amorphous TiO<sub>2</sub> NPs (Figure 5). PDF peaks are tiny at longer radial distances (>5 Å), indicating a lack of long-range order. The first intense peak at 1.8 Å corresponds to the first O shell around Ti atoms. Several PDF peaks at distances less than 4 Å represent a short-range order in nanoparticles.

 $(\text{TiO}_2)_n$  nanoparticles with n = 18, 19, and 20 have diameters in the range of 1.4–1.47 nm (Table 1). The diameter of TiO<sub>2</sub> NPs was calculated by determining the furthest distance and adding the vdW radii of end atoms in the Multiwfn program [75]. The diameter and density of



FIGURE 2: Total energy per atom of the most stable  $(TiO_2)_n$  NPs obtained using the PM6-D3 model and USPEX.



FIGURE 3: The global minimum of  $(TiO_2)_{20}$  NPs using MOPAC as a structural optimizer and USPEX directing the search. Structures optimized with the PM6-D3 model.

nanoparticles follow a similar trend as the cluster size increases (Figure S4). The  $(TiO_2)_{20}$  nanoparticle density is 3.77 g/cm<sup>3</sup>, lower than that of bulk anatase  $(3.90 \text{ g/cm}^3)$ . However, nanoparticles with n = 18 and 19 units present a similar density to bulk anatase, 3.88 and  $3.90 \text{ g/cm}^3$ , respectively.

The relation between the volume (V) and the size (n) of  $(\text{TiO}_2)_n$  NPs presents a linear correlation (Figure 6(b)). As the nanoparticle increases in size, it roughly takes the form of a sphere (Figure 4). The TiO<sub>2</sub> NP diameter follows a fitting  $D(\text{Å}) = 3.21 * \ln (n) + 5.31$ . All nanoparticle diameters determined in this work are smaller than the Bohr radius of anatase and rutile estimated at around 3.9 and 7.7 nm, respectively (Table 2).

3.3. Frenkel Excitons of  $TiO_2$  NPs. As described above, an exciton may be visualized as a couple consisting of an electron and the associated hole, attracted to each other via Coulomb forces. Therefore, such a bound electron-hole pair no longer describes two independent quasiparticles, and its internal energy is lower than its fundamental band gap [83]. Calculating the exciton binding energy of  $TiO_2$  NPs requires knowing the fundamental and the optical gap; see Eq. (5). Their values are presented in Table 3 and Figure 6(d).

There are three basic exciton types: Frenkel exciton or a small-radius exciton, charge transfer exciton, and Wannier exciton or a larger-radius exciton [83]. For the  $TiO_2$  NPs, the Frenkel excitons are relevant since they are highly



FIGURE 4: The most stable  $(TiO_2)_n$  NPs, with  $n \le 20$ , obtained at the PBE0/def2-TZVP level of theory.

localized and are conditioned by the small size of the nanoparticles, 0.8-1.5 nm; see Table 1. This section will discuss the Frenkel excitons in TiO<sub>2</sub> NPs, and the Wannier excitons of bulk anatase and rutile will be addressed afterward.

As the TiO<sub>2</sub> cluster size increases, it is easier for them to accept electrons; hence, their electronic affinity rises. At the same time, it is energetically favorable to remove an electron from TiO<sub>2</sub> NPs, reducing its ionization potential (Figure S5). These two effects cause the fundamental gap to narrow as the nanoparticle grows (Figure 6(d)). The prevalence of sizedependent electronic properties is notable for nanometric materials, including the band gap and the exciton binding energy. These quantities determine the spectroscopy states of the material and its photoelectrochemical properties [15].

Figure S6 and Figure 7 present the UV-vis absorption spectra of  $(\text{TiO}_2)_n$  with n = 5 - 20. The ground state of nanoparticles is a singlet, and only the transitions that obey the selection rule  $\Delta S = 0$  were studied. Therefore, the UV-vis spectrum shows the transitions  $S_0$  to  $S_1$ - $S_5$ ; only

the five lowest excited states were determined by TDDFT. The optical gap corresponds to the energy of the first excited state  $S_1$ . The states  $S_1$  are in the region 293 to 319 nm, corresponding to an energy difference of 0.341 eV. Consequently, the optical gap describes an almost horizontal line concerning the system size (Figure 6(d)).

The first excited states  $S_1$  correspond to  $n \longrightarrow \pi *$  transitions; i.e., for  $(TiO_2)_{20}$ , an electron is promoted from the nonbonding molecular orbital (MO) HOMO-3, corresponding to electron lone pairs from O 2*p* orbitals to empty LUMO (57%) and LUMO + 1 (15%). Ti 3*d* atomic orbitals significantly contribute to these unfilled molecular orbitals; see Figure 7(g). A similar  $n \longrightarrow \pi *$  transition occurs for  $(TiO_2)_{19}$ . These results agree with those reported experimentally by Tang et al. [85]. The interactions between electrons in excited state  $S_1$  differ from those in the ground state  $S_0$ : there is a weaker electron repulsion in  $S_1$  because a pair of electrons can occupy different MO. This decreased electron-electron repulsion gives the exciton binding energy

Cluster size (n)	Point group	d(Ti - O) (Å)	Diameter (Å)	Area (Å <sup>2</sup> )	Volume (Å <sup>3</sup> )	Ti CN	O CN	Density (g/cm <sup>3</sup> )
2	C <sub>2h</sub>	1.744	8.10	134.5	84.7	3.0	1.5	3.13
3	Cs	1.831	8.34	170.5	119.4	3.7	1.8	3.33
4	$C_{2v}$	1.843	8.27	202.1	153.0	4.0	2.0	3.47
5	Cs	1.836	10.21	228.2	188.4	4.0	2.0	3.52
6	$C_2$	1.836	11.07	258.0	224.1	4.0	2.0	3.55
7	Cs	1.828	12.59	287.5	258.4	4.0	2.0	3.59
8	C <sub>2h</sub>	1.819	12.48	310.5	296.8	4.0	2.0	3.57
9	$C_1$	1.847	12.72	338.3	326.8	4.2	2.1	3.65
10	$C_1$	1.839	12.92	357.5	365.3	4.2	2.1	3.63
11	$C_1$	1.836	13.66	380.7	399.7	4.2	2.1	3.65
12	$C_1$	1.834	13.34	400.7	434.0	4.2	2.1	3.67
13	$C_1$	1.874	12.44	407.0	456.0	4.6	2.3	3.78
14	$C_1$	1.842	14.24	439.5	500.6	4.3	2.1	3.71
15	$C_1$	1.846	15.42	461.9	534.6	4.3	2.2	3.72
16	$C_1$	1.843	14.44	495.5	575.0	4.3	2.1	3.69
17	$C_1$	1.856	13.67	490.0	601.1	4.4	2.2	3.75
18	$C_1$	1.894	14.77	490.1	614.7	4.8	2.4	3.88
19	$C_1$	1.911	14.13	510.4	645.8	4.9	2.5	3.90
20	$C_1$	1.857	13.99	543.5	703.7	4.5	2.2	3.77
Anatase	—	1.949 <sup>a</sup>	—	—	—	6.0	3.0	3.90

TABLE 1: Geometrical parameters of TiO2 NPs obtained at the PBE0/def2-TZVP level of theory.

<sup>a</sup>From Ref. [86].



FIGURE 5: Comparison between the theoretical pair distribution function (PDF) of amorphous  $(TiO_2)_n$  NPs with n = 18, 19, and 20.

[15]. Moreover, the quantum confinement effects derive from changes in electron-electron interactions proportional to MO delocalizations. The MO in the states  $S_0$  and  $S_1$  appear more delocalized for n = 19 than for n = 20, reducing the electron-electron interactions. Thus, the optical gap,  $E_{opt}$  (n = 19) = 3.892 eV, is the smallest of nanoparticles with a diameter greater than 1 nm.

The  $E_{\rm B}$  of TiO<sub>2</sub> NPs strongly follows the trend of the fundamental gap  $E_{\rm fund}$ , which diminishes with the nanopar-

ticle size. In contrast, it is unexpected that the optical gap  $E_{opt}$  remains almost constant with the nanoparticle size—at least for the size of the cluster studied here. Thus, the exciton binding energy variation is mainly controlled by reducing the fundamental band gap.

The  $E_{\rm B}$  as a function of size *n* is plotted in Figure 8. The  $E_{\rm B}$  can be fitted by the power law  $E_{\rm B} \sim 1/n^{\alpha}$ , where  $\alpha = 0.85$  for  $(\text{TiO}_2)_n$  NPs; this should be contrasted with the universal 1/R scaling law predicted by the effective mass



FIGURE 6: Continued.



FIGURE 6: Properties of TiO<sub>2</sub> NPs obtained at the PBE0/def2-TZVP level of theory as a function of the cluster size *n*. (a) Average d(Ti - O) bond length; (b) volume for the ground state of  $(TiO_2)_n$ ; (c) diameter of  $(TiO_2)_n$  NPs; (d) the exciton binding energy of  $(TiO_2)_n$  NPs.

TABLE 2: Parameters calculated with the PBE/PAW method for the Wannier exciton model of anatase and rutile using the high-frequency ( $\varepsilon_{\infty}$ ) and static dielectric constants ( $\varepsilon_r$ ).

Phase	Method	$\mu^{a}$				$E_{\rm B}~({\rm meV})^{\rm a}$			- 1-
		$\epsilon_{\infty}$	$\varepsilon_r^{\mathrm{theo}}$	$\varepsilon_r^{\exp}$	$\epsilon_{\infty}$	$\varepsilon_r^{\mathrm{theo}}$	$\varepsilon_r^{\exp}$	(Å)	$a_{\rm x}/a$
Anatase	PBE + U	0.51	0.48	0.44	242.6	13.77	5.81	38.7	10
	PBE	0.41	0.35	0.36	137.6	1.99	4.73	47.6	13
	PBEsol	0.37	0.32	0.32	125.7	2.57	4.28	52.5	14
	Experimental						180 <sup>b</sup>		
Rutile	PBE + U	0.91	0.91	1.16	313.8	8.10	0.55	77.3	26
	PBE	0.85	0.76	1.07	187.1	121.6	0.51	83.4	28
	PBEsol	0.78	1.0	1.00	169.5	0.06	0.47	89.6	30
	Experimental						$4^{c}$		

<sup>a</sup>Reduced effective mass ( $\mu$ ) and  $E_{\rm B}$  calculated using different dielectric constants. <sup>b</sup>Exciton binding energy for direct transition from Ref. [13]. <sup>c</sup>From Ref. [11].

approximation (EMA),  $E_B^{\rm EMA} = C(e^2/\epsilon R)$ , where *C* is a dimensionless constant that only depends on the shape of the QDs and *R* is the dimension of the QDs [16]. In our case,  $R \propto n$ . We obtain a simple relation  $E_{\rm B}$  (eV) = 9.74/*n*; although, a better fitting with the nanoparticle size is obtained when  $\alpha = 0.85$ ,  $E_{\rm B}$  (eV) = 8.07/ $n^{0.85}$ . Moreover,  $E_{\rm B}$  also has a sublinear scaling with the inverse size of quantum dots with size in the range of 1–2.4 nm and  $E_{\rm B} = 54 - 669$  meV: Si ( $\alpha = 0.82$ ), GaAs ( $\alpha = 0.90$ ), and CdSe ( $\alpha = 0.86$ ) [16].

The Bohr radii for the Wannier excitons of anatase and rutile were 3.9 and 7.7 nm, respectively (Table 2). In contrast, the nanoparticle with n = 20 units of TiO<sub>2</sub> only had a radius of 0.7 nm. Due to the size restriction, the excitons in the TiO<sub>2</sub> NPs are localized and correspond to Frenkel excitons. The extension of Wannier excitons prevents their presence in TiO<sub>2</sub> NPs.

Nanoparticles between 1 and 1.5 nm have  $E_{\rm B}$  in the range of 0.132–2.1 eV, indicating a strong dependence on the system size. Even for  $(\text{TiO}_2)_{19}$  with an exciton binding energy of 132 meV, the electron hole will remain correlated

at room temperature. Therefore,  $TiO_2$  NPs with sizes up to 1.5 nm present strongly bound Frenkel excitons.

3.4. Wannier Exciton Model for Anatase and Rutile  $(TiO_2 Crystal Phases)$ . The electron and hole effective masses are responsible for the transport properties in semiconductors. However, the available experimental data suffer from substantial uncertainty due to the difficulty of obtaining them experimentally [78]. Moreover, the calculated values of the effective mass depend on the chosen definition and numerical implementation [99]. For these reasons, we are only interested in reproducing the order of magnitude and the anisotropy of m \* by means of DFT.

Anisotropy can be estimated from the factor  $\eta = \varepsilon_{r,\perp}/\varepsilon_{r,\parallel}$ [79]. Using the experimental values of  $\varepsilon_r$ , we obtain 1.98 and 0.42 for anatase and rutile, respectively. For anatase TiO<sub>2</sub>, all functionals followed the trend  $m_{e,[001]}^* > m_{e,[110]}^*$ , while for rutile, the opposite is observed; this result shows the strong anisotropy of TiO<sub>2</sub>.

TABLE 3: Energetic parameters of  $(\text{TiO}_2)_n$  NPs obtained at the PBE0/def2-TZVP level of theory. Energies in eV.

Cluster size (n)	IP	EA	E <sub>fund</sub>	E <sub>opt</sub>	$E_{\rm B}$
2	9.764	1.508	8.255	4.139	4.116
3	9.630	2.880	6.750	3.629	3.123
4	9.718	2.234	7.485	4.090	3.395
5	9.227	2.972	6.255	4.153	2.102
6	9.276	3.339	5.936	4.240	1.696
7	9.221	3.302	5.919	4.350	1.569
8	9.059	3.150	5.909	4.334	1.575
9	8.993	3.517	5.476	4.391	1.085
10	8.965	3.431 3.6 <sup>b</sup>	5.533	4.398	1.135
11	8.889	3.399	5.490	4.329	1.164
12	8.957	3.508	5.450	4.516	0.934
13	8.843	3.345	5.497	4.220	1.278
14	8.703	3.345	5.358	4.161	1.197
15	8.717 8.57 <sup>d</sup>	4.353	4.364	3.998	0.366
16	8.484	3.987	4.496	4.233	0.263
17	8.353	4.022	4.331	4.005	0.326
18	8.679	3.964	4.716	4.157	0.559
19	8.576	4.552	4.024	3.892	0.132
20	8.504	3.698	4.806	4.129	0.677
TiO <sub>2</sub>	$9.54 \pm 0.10^{a}$ $10.2 \pm 0.2^{c}$	3.9 <sup>e</sup>			
Rutile	7.83 <sup>g</sup>	4.9 <sup>f</sup>	3.0 <sup>i</sup>		
Anatase	8.30 <sup>g</sup> 7.25 <sup>h</sup>	$5.1^{\rm f}$ ~ $4.1^{\rm h}$	3.2 <sup>i</sup>		

<sup>a</sup>Experimental IP obtained by electron impact threshold measurements from Ref. [91]. <sup>b</sup>Experimental adiabatic EA of the  $(TiO_2)_{10}$  neutral system obtained by magnetic-bottle photoelectron spectroscopy (PES) apparatus equipped with a laser vaporization cluster source from Ref. [92]. <sup>c</sup>First IP of TiO<sub>2</sub> from ionization efficiency curves and appearance potentials by electron impact [93]. <sup>d</sup>Theoretical adiabatic IP was obtained for the  $(TiO_2)_{15}$  system from Ref. [28]. <sup>e</sup>Experimental EA of 3.9 eV for the TiO<sub>2</sub> nanoporous films from Ref. [94]. <sup>f</sup>Experimental EA for bulk anatase and rutile by ultraviolet photoelectron spectroscopy (UPS) from Ref. [95]. <sup>g</sup>Theoretical IP using DFT and the screened nonlocal exchange-correlation density functional (HSE06) from Ref. [96]. <sup>h</sup>Experimental IP by photoelectron yield spectra of anatase TiO<sub>2</sub> and EA estimated through the conduction band edge from Ref. [97]. <sup>i</sup>From Ref. [98].

Anatase presents an electronic structure with almost flat bands along the Z- $\Gamma$  direction of the three-dimensional (3D) Brillouin zone (BZ), see Figures S7(a) and S7(b), leading to a high effective electron mass of around 4; see Table 4. Moreover, anatase ( $\Gamma$ -X direction) is more conductive for electrons than the rutile phase (Z- $\Gamma$ direction). This behavior explains why anatase gives better efficiency than rutile for applications where TiO<sub>2</sub> must be a good electron conductor [78, 104]. Table 4 also shows that the effective mass of the hole in anatase is smaller than that in rutile, indicating that the photoexcited charge carriers of anatase more easily migrate to the surface and participate in photocatalytic reactions due to their higher 11

mobility (mobility =  $e\tau/m^*$ ) [105]. Zhang et al. came to the same conclusion but with effective masses one order of magnitude less, showing the effect of the numerical method used [104]. To verify the calculated effective masses, we compared the values obtained with effmass [106] and vaspkit programs [82], which provide similar values.

Even though rutile has a reduced effective mass about two to three times that of anatase, the exciton binding energy is lower due to its high dielectric constant; see Table 2. The static dielectric constant must be determined to calculate the Wannier exciton energy using Eq. (11). For anatase, the PBEsol method was effective in reproducing the experimental values, as shown in Table 4. However, the ionic contributions are more significant in rutile and must be considered when calculating the static dielectric constant. The permittivity in conductive, reduced, or doped TiO<sub>2</sub> rutile is controversial, with reported values in the range of 100-10,000 [103]. According to experimental values, rutile presents a dielectric constant of 110 and 260 at 0K for the perpendicular and longitudinal axes, respectively [102], resulting in a geometric mean of 169, which is about five times that of anatase [32]. The exciton energy is inversely proportional to the square of the dielectric constant for Wannier excitons; this is why rutile exhibits surprisingly low exciton energy of around 4 meV [11]. Additionally, at 50 K, there is sufficient thermal energy  $k_{\rm B}T$  for dissociating the exciton in the rutile TiO2. Hence, the electron-hole pair is uncorrelated at room temperature [11].

Anatase  $\text{TiO}_2$  presents a strongly bound exciton for the direct optical gap. The experimental direct band gap was measured by Baldini et al. [13] using the angle-resolved photoemission spectroscopy, obtaining a value of 3.97 eV. In contrast, the direct optical gap measured by spectroscopy ellipsometry was 3.79 eV, and through Eq. (5), they found an exciton binding energy of 180 meV. This exciton has an intermediate character between the Wannier and Frenkel regimes. However, anatase presents an indirect band gap of 3.2 eV. According to Hall et al. [107], an indirect transition can take place if a phonon is simultaneously created or destroyed, but the transition must meet momentum conservation [104]:

$$E_{q} = \hbar \omega_{\text{photon}}, \qquad (12)$$

$$\hbar k'_e - \hbar k_e = \pm \hbar q_{\rm phonon},\tag{13}$$

where  $\hbar$  is the reduced Plank constant;  $k'_e$  and  $k_e$  are the electron wave vectors at the valence band maximum and conduction band minimum, respectively;  $q_{\rm phonon}$  is the wave vector of the assisted phonon;  $E_g$  is the band gap of the semiconductor; and  $\omega_{\rm photon}$  is the angular frequency of the photon. For anatase,  $k'_e \neq k_e$ ; see Figure S7(a); thus, the transition is assisted by phonons. Therefore, the exciton binding energy for this indirect transition does not correspond to the value of 180 meV. Moreover, the role of the electron-phonon coupling must be considered for the exciton with an indirect optical gap. Table 2 shows



FIGURE 7: UV-vis absorption spectra of  $(\text{TiO}_2)_n$  NPs with n = 15 - 20. (a-f) Vertical lines represent the corresponding lowest transitions from the singlet ground state  $(S_0)$  to excited states  $S_1-S_5$  (shown in relative magnitudes). (g, h) The main contribution of the molecular orbitals (isosurface value = 0.025 a.u.) in the excitation  $S_0 \rightarrow S_1$  of  $(\text{TiO}_2)_{20}$  and  $(\text{TiO}_2)_{19}$ .

uncorrelated electron-hole pairs of about 5 meV for anatase, qualitatively explained by a Wannier exciton model. The rutile exciton is more delocalized than the anatase exciton. Furthermore, anatase presents a Bohr radius in the range of 3–5 nm, which is similar to the Bohr radius of the direct exciton, 3.2 nm [13].

Since the exciton energy is very sensitive to the dielectric constant value, it is essential to obtain theoretical values  $\varepsilon_r$  in

agreement with empirical evidence. As mentioned above, the static dielectric constant ( $\varepsilon_r$ ) has an electron ( $\varepsilon_{\infty}$ ) and an ionic rearrangement ( $\varepsilon_{vib}$ ) contribution. DFT calculates values for high-frequency dielectric constants consistent with experimental data; see Table 2. For example, PBE + *U* has 6% of error. The theoretical determination of the vibrational contribution requires the calculation of the phonon spectrum. However, the VASP code only determines the



FIGURE 8: Exciton binding energy of  $(\text{TiO}_2)_n$  NPs with n = 2 - 20 calculated at the PBE0/def2-TZVP level of theory. Exciton binding energy scales approximately as  $E_B \sim 1/n^{\alpha}$ .

Phase	Mathad	Band gap (eV)	$m_{\rm e} * / m_{\rm e}$		$m_{\rm h} * / m_{\rm e}$		0	0
	Method		[001]	[110]	[001]	[110]	ε <sub>co</sub>	ε <sub>r</sub>
Anatase	PBE + U	2.50	3.92	0.53	1.34	1.82	5.43(⊥) 5.24(  )	25.58(⊥) 18.51(  )
	PBE	2.10	4.15	0.42	1.08	1.48	6.62(⊥) 6.07(  )	72.21(⊥) 32.76(  )
	PBEsol	2.08	3.79	0.41	0.85	1.28	$6.66(\perp)$ 6.08(  )	58.24(⊥) 29.35(  )
	Experimental	3.2 <sup>a</sup>					5.82(⊥) <sup>b</sup> 5.41(  ) <sup>b</sup>	$45.1(\perp)^{b}$ 22.7(  ) <sup>b</sup>
Rutile	PBE + U	2.23	0.76	2.46	3.01	1.85	5.79(⊥) 6.82(  )	36.16(⊥) 42.04(  )
	PBE	1.83	0.60	1.52	5.17	2.88	7.12(⊥) 8.65(  )	9.43(⊥) 8.98(  )
	PBEsol	1.84	0.55	1.48	4.31	2.54	7.23(⊥) 8.64(  )	300.43(⊥) 733.3(  )
	Experimental	3.0 <sup>a</sup>					$6.0(\perp)^{c}$ 7.3(  ) <sup>c</sup>	110(⊥) <sup>d</sup> 260(  ) <sup>d</sup> 240(  ) <sup>e</sup>

TABLE 4: Electronic properties of bulk anatase and rutile obtained with the PBE/PAW level of theory.

<sup>a</sup>From Ref. [98]. <sup>b</sup>From Ref. [100]. <sup>c</sup>From Ref. [101]. <sup>d</sup>From Ref. [102]. <sup>e</sup>From Ref. [103].

phonon frequencies at the  $\Gamma$  point. Hence, the theoretical values of  $\varepsilon_r^{\text{theo}}$  disagree with the experimental ones, especially for the rutile phase. The proposed methodology applies to other systems for calculating the exciton binding energy. When the systems are highly ionic, it is advisable to consider the vibrational dielectric constant. Although this implies an increase in computational cost owing to the need to determine the normal modes of vibration by finite differences numerically, the accuracy gained in the calculation justifies this approach.

As expected, when the high-frequency dielectric constant is used to determine the exciton binding energy, the highest energy unrelaxed exciton is obtained. In the exciton generation, the charge screening experienced by the exciton arises only from the electronic density ( $\varepsilon_{\infty}$ ) since it is faster than atomic motions in the crystal. Hence, the unrelaxed exciton emerges during the exciton generation. Consequently, the atoms move to adapt to the exciton, and the charge screening will be governed by  $\varepsilon_r$ , giving rise to the relaxed exciton [78]. Table 2 presents the unrelaxed and relaxed exciton binding energy, where  $E_{\rm B}(\varepsilon_{\infty}) > E_{\rm B}(\varepsilon_r^{\rm theo}) > E_{\rm B}(\varepsilon_r^{\rm exp})$ . It should be noted that  $E_{\rm B}(\varepsilon_{\infty})$  underestimates the experimental value of the exciton energy for rutile by a factor of 10.

The exciton Bohr radius,  $a_X = (\varepsilon_r/\mu)n^2 a_B$ , is calculated using the experimental dielectric constant  $\varepsilon_r^{exp}$ , n = 1 (ground state), and  $a_B = 0.529$  Å (Table 2). According to  $a_x/a$ , where *a* is the smallest lattice parameter of anatase or rutile, the exciton is delocalized over more than 10 unit cells for anatase and 26 unit cells for rutile, indicating that the exciton experiences the surrounding medium as a homogenous dielectric medium and justifying the use of Wannier's model to compute the exciton binding energy from Eq. (11).

#### 4. Conclusions

This work proposes a methodology to estimate the exciton binding energy of  $(\text{TiO}_2)_n$  nanoparticles with  $n \le 20$ . As a first step, the most stable structures were determined through an evolutionary algorithm.

Gradually increasing the level of theory (PM6-PBE-PBE0) to calculate the total energy of the system allows treating nanoparticles up to 1.4 nm in affordable computational times. Therefore, the evolutionary algorithm USPEX + semiempirical methods + DFT will allow to build TiO<sub>2</sub> nanoparticles up to 2-3 nm. These particle sizes are already relevant for experimental work. The variation operators implemented in the genetic algorithm that produced the most stable structures were heredity (42%) and random (32%). The  $(TiO_2)_n$  nanoparticles with up to 24 atoms (n = 8) show point symmetry, while the remaining ones are amorphous.

The  $(\text{TiO}_2)_n$  nanoparticles exhibit strongly bound Frenkel excitons that scale as  $E_{\text{B}}$  (eV) = 8.07/ $n^{0.85}$ . The exciton binding energy strongly correlates with the nanoparticle size but appears to converge as they grow. The primary factor determining the exciton energy is the fundamental gap.

In TiO<sub>2</sub> nanoparticles, the separation of photogenerated charge carriers should be promoted to increase their lifetime and availability. However, strongly bonded Frenkel excitons impair the performance of TiO<sub>2</sub> in photocatalytic and photovoltaic applications; for example, the 1.4 nm particle presents an  $E_{\rm B} = 0.677$  eV, which prevents it from being useful in photocatalysis.

The Wannier model is adequate to calculate the exciton energy of anatase and rutile in volume. Unlike in TiO<sub>2</sub> nanoparticles, the excitons of rutile (7.7 nm) and anatase (3.9 nm) are delocalized, according to the Bohr radii. The effective masses of anatase are lighter than those of rutile, which explains the higher mobility of the charge carriers of anatase. Higher mobility is essential for indirect gap semiconductors such as anatase. The exciton binding energy of rutile (4 meV) contrasts with those present in nanoparticles around 1.4 nm (0.132-1.2 eV). That is, for Frenkel excitons (~1.4 nm), the  $E_{\rm B}$  (eV) = C/ $\varepsilon n^{0.85}$ , while in bulk material,  $E_{\rm B}$  (eV) = 13.61 \*  $\mu/\varepsilon^2$ .

#### **Data Availability**

All data used to support the findings of this study are included within the article.

#### **Conflicts of Interest**

The authors declare that there is no conflict of interest regarding the publication of this article.

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#### **Supplementary Materials**

Table S1: statistics for each  $(\text{TiO}_2)_n$  NP using the PM6-D3 model implemented in MOPAC as a structural optimizer and the USPEX program. Figure S1: coordination number of  $(\text{TiO}_2)_n$  NPs with n = 18, 19, and 20. Figure S2: polyhedra of TiO<sub>2</sub> NPs. (a)  $(\text{TiO}_2)_{20}$ , (b)  $(\text{TiO}_2)_{19}$ , and (c)  $(\text{TiO}_2)_{18}$ . Figure S3: XRD pattern of the amorphous  $(\text{TiO}_2)_{20}$  NPs. Figure S4: the diameter and density of  $(\text{TiO}_2)_n$  NPs. Figure S5: ionization potential (IP) and electron affinity (EA) of TiO<sub>2</sub> NPs obtained at the PBE0/def2-TZVP level of theory. Figure S6: UV-vis absorption spectra of  $(\text{TiO}_2)_n$  NPs with n = 5 - 14. Figure S7: (a) band structure calculation of anatase TiO<sub>2</sub> using the PBE functional. Figure S8: (a) band structure calculation of rutile TiO<sub>2</sub> using the PBE functional. (*Supplementary Materials*)

#### References

- M. A. Vargas and J. E. Rodríguez-Páez, "Amorphous TiO<sub>2</sub> nanoparticles: synthesis and antibacterial capacity," *Journal* of Non-Crystalline Solids, vol. 459, pp. 192–205, 2017.
- [2] A. Kusior, J. Banas, A. Trenczek-Zajac, P. Zubrzycka, A. Micek-Ilnicka, and M. Radecka, "Structural properties of TiO<sub>2</sub> nanomaterials," *Journal of Molecular Structure*, vol. 1157, pp. 327–336, 2018.
- [3] V. M. Ramakrishnan, M. Natarajan, A. Santhanam, V. Asokan, and D. Velauthapillai, "Size controlled synthesis of TiO<sub>2</sub> nanoparticles by modified solvothermal method towards effective photo catalytic and photovoltaic applications," *Materials Research Bulletin*, vol. 97, pp. 351–360, 2018.
- [4] R. Singh and S. Dutta, "Synthesis and characterization of solar photoactive TiO<sub>2</sub> nanoparticles with enhanced structural and optical properties," *Advanced Powder Technology*, vol. 29, no. 2, pp. 211–219, 2018.
- [5] K. Manjunath, L. S. Reddy Yadav, T. Jayalakshmi, V. Reddy, H. Rajanaika, and G. Nagaraju, "Ionic liquid assisted hydrothermal synthesis of TiO<sub>2</sub> nanoparticles: photocatalytic and antibacterial activity," *Journal of Materials Research and Technology*, vol. 7, no. 1, pp. 7–13, 2018.
- [6] G. Nagaraj, A. Dhayal Raj, and A. Albert Irudayaraj, "Next generation of pure titania nanoparticles for enhanced solarlight photocatalytic activity," *Journal of Materials Science: Materials in Electronics*, vol. 29, no. 5, pp. 4373–4381, 2018.

- [7] C.-Y. Wu, K. J. Tu, J. P. Deng, Y. S. Lo, and C. H. Wu, "Markedly enhanced surface hydroxyl groups of TiO<sub>2</sub> nanoparticles with superior water-dispersibility for photocatalysis," *Materials*, vol. 10, no. 5, p. 566, 2017.
- [8] H. Lin, C. P. Huang, W. Li, C. Ni, S. I. Shah, and Y.-H. Tseng, "Size dependency of nanocrystalline TiO<sub>2</sub> on its optical property and photocatalytic reactivity exemplified by 2chlorophenol," *Applied Catalysis B: Environmental*, vol. 68, no. 1-2, pp. 1–11, 2006.
- [9] N. Serpone, D. Lawless, and R. Khairutdinov, "Size effects on the photophysical properties of colloidal anatase TiO<sub>2</sub> particles: size quantization versus direct transitions in this indirect semiconductor?," *The Journal of Physical Chemistry*, vol. 99, no. 45, pp. 16646–16654, 1995.
- [10] J.-L. Bredas, "Mind the gap!," *Materials Horizons*, vol. 1, no. 1, pp. 17–19, 2014.
- [11] J. Pascual, J. Camassel, and H. Mathieu, "Fine structure in the intrinsic absorption edge of TiO<sub>2</sub>," *Physical Review B*, vol. 18, no. 10, pp. 5606–5614, 1978.
- [12] A. Amtout and R. Leonelli, "Time-resolved photoluminescence from excitons in TiO<sub>2</sub>," *Solid State Communications*, vol. 84, no. 3, pp. 349–352, 1992.
- [13] E. Baldini, L. Chiodo, A. Dominguez et al., "Strongly bound excitons in anatase TiO<sub>2</sub> single crystals and nanoparticles," *Nature Communications*, vol. 8, no. 1, pp. 13–13, 2017.
- [14] L. Chiodo, J. M. García-Lastra, A. Iacomino et al., "Selfenergy and excitonic effects in the electronic and optical properties of TiO<sub>2</sub> crystalline phases," *Physical Review B*, vol. 82, no. 4, article 045207, 2010.
- [15] G. D. Scholes and G. Rumbles, "Excitons in nanoscale systems," *Nature Materials*, vol. 5, no. 9, pp. 683–696, 2006.
- [16] A. Franceschetti and A. Zunger, "Direct pseudopotential calculation of exciton Coulomb and exchange energies in semiconductor quantum dots," *Physical Review Letters*, vol. 78, no. 5, pp. 915–918, 1997.
- [17] B. A. Gregg, "Excitonic solar cells," *The Journal of Physical Chemistry B*, vol. 107, no. 20, pp. 4688–4698, 2003.
- [18] V. D'Innocenzo, G. Grancini, M. J. P. Alcocer et al., "Excitons versus free charges in organo-lead tri-halide perovskites," *Nature Communications*, vol. 5, no. 1, p. 3586, 2014.
- [19] L. Chiodo, M. Salazar, A. H. Romero, S. Laricchia, F. D. Sala, and A. Rubio, "Structure, electronic, and optical properties of TiO<sub>2</sub> atomic clusters: an *ab initio* study," *The Journal of Chemical Physics*, vol. 135, no. 24, article 244704, 2011.
- [20] M. L. Weichman, X. Song, M. R. Fagiani et al., "Gas phase vibrational spectroscopy of cold  $(\text{TiO}_2)_n^-$  (n = 3 8) clusters," *The Journal of Chemical Physics*, vol. 144, no. 12, article 124308, 2016.
- [21] F. Aguilera-Granja, A. Vega, and L. C. Balbás, "New structural and electronic properties of (TiO<sub>2</sub>)<sub>10</sub>," *The Journal of Chemical Physics*, vol. 144, no. 23, article 234312, 2016.
- [22] L. Tang, L. Sai, J. Zhao, and R. Qiu, "A topological method for global optimization of clusters: application to  $(TiO_2)_n$  (n = 1 6)," *Journal of Computational Chemistry*, vol. 33, no. 2, pp. 163–169, 2012.
- [23] A. Mohajeri and F. Haghshenas, "Global reactivity and site selectivity of  $(TiO_2)_n$  nanoclusters (n = 5 10) toward hydrogen peroxide," *Materials Chemistry and Physics*, vol. 183, pp. 326–333, 2016.
- [24] D. Cho, K. C. Ko, O. Lamiel-García, S. T. Bromley, J. Y. Lee, and F. Illas, "Effect of size and structure on the ground-state

and excited-state electronic structure of TiO<sub>2</sub> nanoparticles," *Journal of Chemical Theory and Computation*, vol. 12, no. 8, pp. 3751–3763, 2016.

- [25] R. B. Wang, S. Körbel, S. Saha, S. Botti, and N. V. Skorodumova, "Structure and optical properties of small (TiO<sub>2</sub>)<sub>n</sub> nanoparticles, n = 21 – 24," *The Journal of Physical Chemistry C*, vol. 121, no. 17, pp. 9528–9536, 2017.
- [26] O. Lamiel-Garcia, A. Cuko, M. Calatayud, F. Illas, and S. T. Bromley, "Predicting size-dependent emergence of crystallinity in nanomaterials: titania nanoclusters versus nanocrystals," *Nanoscale*, vol. 9, no. 3, pp. 1049–1058, 2017.
- [27] Z.-w. Qu and G.-J. Kroes, "Theoretical study of the electronic structure and stability of titanium dioxide clusters  $(\text{TiO}_2)_n$  with n = 1 9," *The Journal of Physical Chemistry B*, vol. 110, no. 18, pp. 8998–9007, 2006.
- [28] Z.-w. Qu and G.-J. Kroes, "Theoretical study of stable, defectfree  $(TiO_2)_n$  nanoparticles with n = 10 - 16," *The Journal of Physical Chemistry C*, vol. 111, no. 45, pp. 16808–16817, 2007.
- [29] S. Li and D. A. Dixon, "Molecular structures and energetics of the  $(TiO_2)_n$  (n = 1 4) clusters and their anions," *The Journal of Physical Chemistry A*, vol. 112, no. 29, pp. 6646–6666, 2008.
- [30] M. Calatayud, L. Maldonado, and C. Minot, "Reactivity of  $(\text{TiO}_2)_N$  clusters (N = 1 10): probing gas-phase acidity and basicity properties," *The Journal of Physical Chemistry C*, vol. 112, no. 41, pp. 16087–16095, 2008.
- [31] E. Berardo, F. Kaplan, K. Bhaskaran-Nair et al., "Benchmarking the fundamental electronic properties of small TiO<sub>2</sub> nanoclusters by GW and coupled cluster theory calculations," *Journal of Chemical Theory and Computation*, vol. 13, no. 8, pp. 3814–3828, 2017.
- [32] N. Marom, M. Kim, and J. R. Chelikowsky, "Structure selection based on high vertical electron affinity for TiO<sub>2</sub> clusters," *Physical Review Letters*, vol. 108, no. 10, article 106801, 2012.
- [33] L. Hung, K. Baishya, and S. Öğüt, "First-principles real-space study of electronic and optical excitations in rutileTiO<sub>2</sub> nanocrystals," *Physical Review B*, vol. 90, no. 16, article 165424, 2014.
- [34] E. Berardo, H.-S. Hu, S. A. Shevlin, S. M. Woodley, K. Kowalski, and M. A. Zwijnenburg, "Modeling excited states in TiO<sub>2</sub> nanoparticles: on the accuracy of a TD-DFT based description," *Journal of Chemical Theory and Computation*, vol. 10, no. 3, pp. 1189–1199, 2014.
- [35] S. A. Shevlin and S. M. Woodley, "Electronic and optical properties of doped and undoped (TiO<sub>2</sub>)n nanoparticles," *The Journal of Physical Chemistry C*, vol. 114, no. 41, pp. 17333–17343, 2010.
- [36] R. Valero, Á. Morales-García, and F. Illas, "Theoretical modeling of electronic excitations of gas-phase and solvated TiO<sub>2</sub> nanoclusters and nanoparticles of interest in photocatalysis," *Journal of Chemical Theory and Computation*, vol. 14, no. 8, pp. 4391–4404, 2018.
- [37] E. Berardo, H.-S. Hu, H. J. J. van Dam et al., "Describing excited state relaxation and localization in TiO<sub>2</sub> nanoparticles using TD-DFT," *Journal of Chemical Theory and Computation*, vol. 10, no. 12, pp. 5538–5548, 2014.
- [38] E. Inclan, D. Geohegan, and M. Yoon, "A hybrid optimization algorithm to explore atomic configurations of TiO<sub>2</sub> nanoparticles," *Computational Materials Science*, vol. 141, pp. 1–9, 2018.

- [39] M. Chen and D. A. Dixon, "Tree growth—hybrid genetic algorithm for predicting the structure of small (TiO<sub>2</sub>)<sub>n</sub>, n = 2 - 13, nanoclusters," *Journal of Chemical Theory and Computation*, vol. 9, no. 7, pp. 3189–3200, 2013.
- [40] S. Hamad, C. R. A. Catlow, S. M. Woodley, S. Lago, and J. A. Mejías, "Structure and stability of small TiO<sub>2</sub> nanoparticles," *The Journal of Physical Chemistry B*, vol. 109, no. 33, pp. 15741–15748, 2005.
- [41] J. P. Perdew, "Density functional theory and the band gap problem," *International Journal of Quantum Chemistry*, vol. 28, no. S19, pp. 497–523, 1985.
- [42] J. C. González-Torres, L. A. Cipriano, E. Poulain, V. Domínguez-Soria, R. García-Cruz, and O. Olvera-Neria, "Optical properties of anatase TiO<sub>2</sub>: synergy between transition metal doping and oxygen vacancies," *Journal of Molecular Modeling*, vol. 24, no. 10, p. 276, 2018.
- [43] J. C. González-Torres, E. Poulain, V. Domínguez-Soria, R. García-Cruz, and O. Olvera-Neria, "C-, N-, S-, and Fdoped anatase TiO<sub>2</sub> (101) with oxygen vacancies: photocatalysts active in the visible region," *International Journal of Photoenergy*, vol. 2018, Article ID 7506151, 12 pages, 2018.
- [44] M. E. Casida and M. Huix-Rotllant, "Progress in timedependent density-functional theory," *Annual Review of Physical Chemistry*, vol. 63, no. 1, pp. 287–323, 2012.
- [45] L. González, D. Escudero, and L. Serrano-Andrés, "Progress and challenges in the calculation of electronic excited states," *ChemPhysChem*, vol. 13, no. 1, pp. 28–51, 2012.
- [46] V. Turkowski, A. Leonardo, and C. A. Ullrich, "Timedependent density-functional approach for exciton binding energies," *Physical Review B*, vol. 79, no. 23, article 233201, 2009.
- [47] A. R. Oganov and C. W. Glass, "Crystal structure prediction using ab initio evolutionary techniques: principles and applications," *The Journal of Chemical Physics*, vol. 124, no. 24, article 244704, 2006.
- [48] A. R. Oganov, A. O. Lyakhov, and M. Valle, "How evolutionary crystal structure prediction works—and why," *Accounts* of Chemical Research, vol. 44, no. 3, pp. 227–237, 2011.
- [49] A. O. Lyakhov, A. R. Oganov, H. T. Stokes, and Q. Zhu, "New developments in evolutionary structure prediction algorithm USPEX," *Computer Physics Communications*, vol. 184, no. 4, pp. 1172–1182, 2013.
- [50] C. W. Glass, A. R. Oganov, and N. Hansen, "USPEX—evolutionary crystal structure prediction," *Computer Physics Communications*, vol. 175, no. 11-12, pp. 713–720, 2006.
- [51] J. J. P. Stewart, MOPAC, Stewart Computational Chemistry, Colorado Springs, CO, USA, 2012.
- [52] J. J. P. Stewart, "Optimization of parameters for semiempirical methods VI: more modifications to the NDDO approximations and re-optimization of parameters," *Journal of Molecular Modeling*, vol. 19, no. 1, pp. 1–32, 2013.
- [53] A. R. Oganov, Modern Methods of Crystal Structure Prediction, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2011.
- [54] A. O. Lyakhov and A. R. Oganov, "Evolutionary search for superhard materials: methodology and applications to forms of carbon and TiO<sub>2</sub>," *Physical Review B*, vol. 84, no. 9, article 092103, 2011.
- [55] J. Zemann, "Crystal structures, 2nd edition. Vol. 1 by R. W. G. Wyckoff," *Acta Crystallographica*, vol. 18, no. 1, pp. 139– 139, 1965.

- [56] U. Diebold, "The surface science of titanium dioxide," *Surface Science Reports*, vol. 48, no. 5-8, pp. 53–229, 2003.
- [57] D. R. Lide, CRC Handbook of Chemistry and Physics, 90th Edition, CRC Press/Taylor and Francis, Boca Raton, FL, 2010.
- [58] S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, "A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu," *The Journal of Chemical Physics*, vol. 132, no. 15, article 154104, 2010.
- [59] G. Kresse and J. Furthmüller, "Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set," *Computational Materials Science*, vol. 6, no. 1, pp. 15–50, 1996.
- [60] P. Hohenberg and W. Kohn, "Inhomogeneous electron gas," *Physical Review*, vol. 136, no. 3B, pp. B864–B871, 1964.
- [61] W. Kohn and L. J. Sham, "Self-consistent equations including exchange and correlation effects," *Physical Review*, vol. 140, no. 4A, pp. A1133–A1138, 1965.
- [62] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," *Physical Review Letters*, vol. 77, no. 18, pp. 3865–3868, 1996.
- [63] P. E. Blöchl, "Projector augmented-wave method," *Physical Review B*, vol. 50, no. 24, pp. 17953–17979, 1994.
- [64] G. Kresse and D. Joubert, "From ultrasoft pseudopotentials to the projector augmented-wave method," *Physical Review B*, vol. 59, no. 3, pp. 1758–1775, 1999.
- [65] F. Neese, "The ORCA program system," Wiley Interdisciplinary Reviews: Computational Molecular Science, vol. 2, no. 1, pp. 73–78, 2012.
- [66] J. P. Perdew, M. Ernzerhof, and K. Burke, "Rationale for mixing exact exchange with density functional approximations," *The Journal of Chemical Physics*, vol. 105, no. 22, pp. 9982– 9985, 1996.
- [67] M. Dolg, U. Wedig, H. Stoll, and H. Preuss, "Energy-adjusted ab initio pseudopotentials for the first row transition elements," *The Journal of Chemical Physics*, vol. 86, no. 2, pp. 866–872, 1987.
- [68] A. Bergner, M. Dolg, W. Küchle, H. Stoll, and H. Preuß, "Ab initio energy-adjusted pseudopotentials for elements of groups 13–17," *Molecular Physics*, vol. 80, no. 6, pp. 1431– 1441, 1993.
- [69] F. Weigend and R. Ahlrichs, "Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: design and assessment of accuracy," *Physical Chemistry Chemical Physics*, vol. 7, no. 18, pp. 3297–3305, 2005.
- [70] F. Weigend, "Accurate Coulomb-fitting basis sets for H to Rn," *Physical Chemistry Chemical Physics*, vol. 8, no. 9, pp. 1057–1065, 2006.
- [71] M. A. L. Marques and E. K. U. Gross, "Time-dependent density functional theory," *Annual Review of Physical Chemistry*, vol. 55, no. 1, pp. 427–455, 2004.
- [72] M. E. Casida, "Time-dependent density functional response theory for molecules," in *Recent Advances in Density Functional Methods*, pp. 155–192, World Scientific, 1995.
- [73] S. M. Dancoff, "Non-adiabatic meson theory of nuclear forces," *Physical Review*, vol. 78, no. 4, pp. 382–385, 1950.
- [74] I. Tamm, "Relativistic interaction of elementary particles," *Journal of Physics (Moscow)*, vol. 9, p. 449, 1945.

- [75] T. Lu and F. Chen, "Multiwfn: a multifunctional wavefunction analyzer," *Journal of Computational Chemistry*, vol. 33, no. 5, pp. 580–592, 2012.
- [76] "Debyer program," 2021, https://github.com/wojdyr/debyer.
- [77] A. Pedretti, L. Villa, and G. Vistoli, "VEGA: a versatile program to convert, handle and visualize molecular structure on Windows-based PCs," *Journal of Molecular Graphics and Modelling*, vol. 21, no. 1, pp. 47–49, 2002.
- [78] T. Le Bahers, M. Rérat, and P. Sautet, "Semiconductors used in photovoltaic and photocatalytic devices: assessing fundamental properties from DFT," *The Journal of Physical Chemistry C*, vol. 118, no. 12, pp. 5997–6008, 2014.
- [79] A. V. Rodina, M. Dietrich, A. Göldner et al., "Free excitons in wurtzite GaN," *Physical Review B*, vol. 64, no. 11, article 115204, 2001.
- [80] J. P. Perdew, A. Ruzsinszky, G. I. Csonka et al., "Restoring the density-gradient expansion for exchange in solids and surfaces," *Physical Review Letters*, vol. 100, no. 13, article 136406, 2008.
- [81] F. Brivio, J. M. Frost, J. M. Skelton et al., "Lattice dynamics and vibrational spectra of the orthorhombic, tetragonal, and cubic phases of methylammonium lead iodide," *Physical Review B*, vol. 92, no. 14, article 144308, 2015.
- [82] V. Wang, N. Xu, J.-C. Liu, G. Tang, and W.-T. Geng, "VASP-KIT: a user-friendly interface facilitating high-throughput computing and analysis using VASP code," *Computer Physics Communications*, vol. 267, article 108033, 2021.
- [83] I. Pelant and J. Valenta, Luminescence Spectroscopy of Semiconductors, Oxford University Press Inc., New York, 2012.
- [84] O. Olvera-Neria, *TiO<sub>2</sub> nanoparticles*, 2022, https://github .com/oscolv/TiO2-nanoparticles.
- [85] H. Tang, H. Berger, P. E. Schmid, and F. Lévy, "Optical properties of anatase (TiO<sub>2</sub>)," *Solid State Communications*, vol. 92, no. 3, pp. 267–271, 1994.
- [86] M. Horn, C. F. Schwebdtfeger, and E. P. Meagher, "Refinement of the structure of anatase at several temperatures," *Zeitschrift für Kristallographie*, vol. 136, no. 3-4, pp. 273– 281, 1972.
- [87] L. X. Chen, T. Rajh, Z. Wang, and M. C. Thurnauer, "XAFS studies of surface structures of TiO<sub>2</sub> nanoparticles and photocatalytic reduction of metal ions," *The Journal of Physical Chemistry B*, vol. 101, no. 50, pp. 10688–10697, 1997.
- [88] K. L. Yeung, A. J. Maira, J. Stolz et al., "Ensemble effects in nanostructured TiO<sub>2</sub> used in the gas-phase photooxidation of trichloroethylene," *The Journal of Physical Chemistry B*, vol. 106, no. 18, pp. 4608–4616, 2002.
- [89] M. Fernández-García, C. Belver, J. C. Hanson, X. Wang, and J. A. Rodriguez, "Anatase-TiO<sub>2</sub> nanomaterials: analysis of key parameters controlling crystallization," *Journal of the American Chemical Society*, vol. 129, no. 44, pp. 13604–13612, 2007.
- [90] H. Zhang, B. Chen, J. F. Banfield, and G. A. Waychunas, "Atomic structure of nanometer-sized amorphous TiO<sub>2</sub>," *Physical Review B*, vol. 78, no. 21, article 214106, 2008.
- [91] D. L. Hildenbrand, "Mass spectrometric studies of the thermochemistry of gaseous TiO and TiO<sub>2</sub>," *Chemical Physics Letters*, vol. 44, no. 2, pp. 281–284, 1976.
- [92] H.-J. Zhai and L.-S. Wang, "Probing the electronic structure and band gap evolution of titanium oxide clusters  $(\text{TiO}_2)_n^{-1}$ (n = 1 - 10) using photoelectron spectroscopy," *Journal of the American Chemical Society*, vol. 129, no. 10, pp. 3022– 3026, 2007.

- [93] E. G. Rauh and R. J. Ackermann, "First ionization potentials of some refractory oxide vapors," *The Journal of Chemical Physics*, vol. 60, no. 4, pp. 1396–1400, 1974.
- [94] R. Könenkamp and I. Rieck, "Electrical properties of Schottky diodes on nano-porous TiO<sub>2</sub> films," *Materials Science and Engineering: B*, vol. 69-70, pp. 519–521, 2000.
- [95] G. Xiong, R. Shao, T. C. Droubay et al., "Photoemission electron microscopy of TiO<sub>2</sub> anatase films embedded with rutile nanocrystals," *Advanced Functional Materials*, vol. 17, no. 13, pp. 2133–2138, 2007.
- [96] D. O. Scanlon, C. W. Dunnill, J. Buckeridge et al., "Band alignment of rutile and anatase TiO<sub>2</sub>," *Nature Materials*, vol. 12, no. 9, pp. 798–801, 2013.
- [97] J.-i. Fujisawa, T. Eda, and M. Hanaya, "Comparative study of conduction-band and valence-band edges of TiO<sub>2</sub>, SrTiO<sub>3</sub>, and BaTiO<sub>3</sub> by ionization potential measurements," *Chemical Physics Letters*, vol. 685, pp. 23–26, 2017.
- [98] L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz, and H. J. Scheel, "Electrochemical and photoelectrochemical investigation of single-crystal anatase," *Journal of the American Chemical Society*, vol. 118, no. 28, pp. 6716–6723, 1996.
- [99] L. D. Whalley, J. M. Frost, B. J. Morgan, and A. Walsh, "Impact of nonparabolic electronic band structure on the optical and transport properties of photovoltaic materials," *Physical Review B*, vol. 99, no. 8, article 085207, 2019.
- [100] R. J. Gonzalez, R. Zallen, and H. Berger, "Infrared reflectivity and lattice fundamentals in anatase TiO<sub>2</sub>s," *Physical Review B*, vol. 55, no. 11, pp. 7014–7017, 1997.
- [101] M. Bass, Optical Properties of Materials, Nonlinear Optics, Quantum Optics, vol. IVMc Graw Hill, 3 edition, 2010.
- [102] R. A. Parker, "Static dielectric constant of rutile TiO<sub>2</sub>, 1.6-1060°K," *Physical Review*, vol. 124, no. 6, pp. 1719–1722, 1961.
- [103] J. Bonkerud, C. Zimmermann, P. M. Weiser, L. Vines, and E. V. Monakhov, "On the permittivity of titanium dioxide," *Scientific Reports*, vol. 11, no. 1, article 12443, 2021.
- [104] J. Zhang, P. Zhou, J. Liu, and J. Yu, "New understanding of the difference of photocatalytic activity among anatase, rutile and brookite TiO<sub>2</sub>," *Physical Chemistry Chemical Physics*, vol. 16, no. 38, pp. 20382–20386, 2014.
- [105] H. Tang, K. Prasad, R. Sanjinès, P. E. Schmid, and F. Lévy, "Electrical and optical properties of TiO<sub>2</sub> anatase thin films," *Journal of Applied Physics*, vol. 75, no. 4, pp. 2042–2047, 1994.
- [106] L. D. Whalley, "effmass: an effective mass package," *Journal of Open Source Software*, vol. 3, no. 28, p. 797, 2018.
- [107] L. H. Hall, J. Bardeen, and F. J. Blatt, "Infrared absorption spectrum of germanium," *Physical Review*, vol. 95, no. 2, pp. 559-560, 1954.