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(Article begins on next page)

Direct measurement and modeling of spontaneous charge

migration~~transfer~~ across anatase–brookite

nanoheterojunctions

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ABSTRACT: Nanocomposites are at the heart of the present nanotechnology revolution in several strategic fields, including Green Chemistry, sensors and pollutant remediation. The promising and extensively examined nanotitania photocatalysts have performances hampered by the rapid recombination of photogenerated charge carriers. To better understand these materials, here we ~~By generalizing~~ the 2D–heterojunctions physics to 3D patchworks of intimately associated anatase and brookite mixed crystallites, i.e. synthesized–multi-phase polymorphs, MPP ~~we explain how this major limitation can be overcome~~. The synthesized anatase/brookite composite material is fully characterized experimentally and by simulations. We demonstrate ~~find~~ that the anatase–brookite interphase behaves ~~at the level of valence bands~~ as a ground–state nano-diode containing an almost ideal nanocapacitor, associated to a net migration ~~transfer~~ of electrons from anatase to brookite ~~for the ground electronic state~~. Implications of the direct observation of a polarized interphase on the understanding of nanotitania photocatalysts at the atomic scale are discussed.

Introduction

The spontaneous recombination of photogenerated charge carriers is the main drawback that impacts negatively on the performances of photocatalytic materials,^{1–4} especially in promising titania-based nanocrystals.^{5,6} In this respect, extrinsic bulk impurity/defect states play a fundamental role,^{5,7,8} as they can create shallow mid-gap states and reduce the apparent bandgap⁹ at the expense of increasing the concentration of trapping centres¹⁰ for electrons (e^-) and holes (h^+), which slow down the recombination rate.¹¹ Crystals of TiO₂ anatase can be also doped on their growing surfaces, to stabilize the metastable {001} facets over the thermodynamically favored, but less reactive, {101} ones.^{12–14} However, neither doping or co-doping has turned pristine titania materials into efficient visible light catalyz~~er~~.^{15,16} These approaches alone have been not proven to be

particularly useful, which has led to the proposal of third generation materials consisting of either two or three interconnected semiconductor materials.^{17–19}

~~Consequently, a~~ In particular, an alternative strategy to fight the curse of recombination relies on hybrid materials,^{20,21} where different semiconductors are joined through a 2D–heterojunction,²² which spontaneously promotes a net flow of charge across the interface.^{23,24} This is due to the thermodynamic drive toward the equilibration of the chemical potential of the two phases, under the continuity constraints imposed by the Poisson’s equation.²⁵ The resulting quantum mechanical picture is that one of a 2D quantum well that traps some charge carriers at the junction, and produces an equilibrium electric double layer.²⁶ Any further migration~~transfer~~ of electrons or holes across the phase boundaries is thus kinetically and thermodynamically hindered and t–he charge vectorial displacement originated from the contact between phases is correlated to the e^-h^+ recombination delay. A variety of layered photonic devices relying on this physics is well known, including light emitting diodes,²⁷ laser diodes,²⁸ photocatalysts,²⁴ and electro–analytical sensors.²⁹

Results and Discussion

~~Due to its fundamental nature, we believe that the nano-diode-like heterojunction, i.e. the charge vectorial displacement originated from the contact between phases is correlated to the e^-h^+ recombination delay.~~ Specifically, even an interface between polymorphs of the same chemical system, like anatase and brookite phases of TiO_2 , can act as a diode, as the valence and conduction band edges of the two bulk crystals are different.³⁰ However, the difference is often too small to be of any practical utility in macroscopic layered devices, which in fact are mostly composed by chemically different compounds³¹.

Here we investigate with atomistic details that nano double–layers in multiphase nanostructured powders of TiO_2 that might be exploited to boost the photocatalytic performances even in the absence of a composite (multi–layered) architecture. It has been substantiated again and again that

heterogeneous mixtures of TiO₂ polymorphs with a predominance of anatase generally show greater photocatalytic yields than one-phase TiO₂ (See Section S7 SI).^{32–35} Specifically, the photocatalytic visible-light performances of N-doped anatase are significantly enhanced in the presence of the brookite phase, even respect to the rutile one^{36–38}. This has been explained by invoking a lower recombination rate of charge carriers, which in turn has been attributed to band alignment effects, and a charge migration~~transfer~~ across the phase boundaries.^{39–41} However, this could be just part of the story. The intimate connection among nanocrystallites of anatase and brookite in well-defined ratios, i.e. nano-diode-like heterojunctions, might cooperatively produce a net measurable equilibrium (ground-state) effect. In other words, we look for “multi-phase polymorphs” (MPP) nano-diodes. The latter are expected to spontaneously self-assemble between surfaces with similar meshes, such as the most stable (101)_{anatase} and (210)_{brookite} facets, which have almost commensurate translation periods (see below and Section S3.3 SI). To this end, we synthesized, characterized and tested multiple nanoheterojunctions in bulk N-doped anatase-brookite TiO₂ nanostructured powders ~~have been synthesized, characterized and tested~~ (details of the experimental procedures are reported in Methods – see below – and in Section S1 of the Supplementary Information; SI). These materials afford an ideal test case to probe the role of the phase composition, as nanopowders with nm-size crystallites bear a very small concentration of bulk grain boundaries that may act as recombination centres,⁴² and surface band bending is negligible.⁴³ In our experiments, ~~T~~the main roles of the non-metal N dopant are (i) to provide the visible light chromophore center and (ii) to control the amount of brookite: the higher the nominal N/Ti molar ratio, the higher the anatase content.^{9,44} We show both experimental and computational evidences that statistically dispersed MPP nano-heterojunctions can cooperatively produce an effective capacitor layer. We also investigated by Principal Component Analysis (PCA) how this may be correlated to the significantly improved photocatalytic performances of the material under UV illumination.

The paper is organized as follows. First, the equilibrium properties of the electronic ground-state system are described based on the outcomes of high-grade DFT simulations and Electrochemical Impedance Spectroscopy measurements in the dark. Then, the response of the system is probed by photocurrent experiments under UV illumination and PCA is performed to find relevant correlations among structural and composition parameters and recombination times. A final section summarizes the main findings and conclusions.

Results and Discussion

Explicit DFT modelling of the anatase:brookite main interface

Semiconductors with very similar band gaps and type (anatase: ~ 3.1 eV; brookite: ~ 3.3 eV) ~~are connected in a manner that supersedes the now beaten path of conventional 2D macroscopic heterojunctions.~~ were chosen to ~~The idea is to~~ create extremely intimate surface contacts of complex 3D networks of statistically oriented nanocrystallites (Figure 1a), in contrast to the artificial ones where the contact is created *ad hoc* on cm^2 -scale surfaces. HR-TEM analyses (Figure 1a and Section S2 SI) demonstrate that the contact between the two phases generated in this way occurs frequently through the association of the most stable^{14,45} $\{101\}_{\text{Anatase}}$ and $\{210\}_{\text{Brookite}}$ facets. In particular, the electron diffraction of the overlapping portion of the two phases reveals the existence of $\{101\}_{\text{Anatase}}:\{210\}_{\text{Brookite}}$ nano-junctions among the nanocrystals. The electron diffraction pattern of the interphase region (Figure 1a, inset**b**) is the superimposition of the diffraction images ascribable to either (101) anatase and/or (210) brookite exposed planes. The corresponding meshes are very similar but differently oriented⁴⁶. As shown in the SI (Sections S3.3 and S3.4), the 1x1 (210) brookite mesh is almost commensurate with a reconstructed 2x1 (101) anatase one, provided that the surfaces are mutually rotated by ~ 10 deg around the non-

crystallographic direction. This implies that the reconstructed (101) anatase surface could serve as a template for the epitaxial growth of (210) brookite (Figure 1b and S5 SI); the energy gain due to brookite crystallization⁴⁷ is more than enough to pay the cost of the reconstruction at the interface, as indicated by the fact the simulations find stable geometries. The large amount of (101):(210) contacts found by the HR-TEM analysis (see also Figure S1 SI), as well as the measured macroscopic capacitance (see below), suggest that such an intimate connection is more frequent than expected on a pure statistical basis. This can be explained by the relative abundance of the most stable $\{101\}_{\text{Anatase}}$ and $\{210\}_{\text{Brookite}}$ surfaces, possibly coupled through an epitaxy-driven heterogeneous nucleation mechanism.

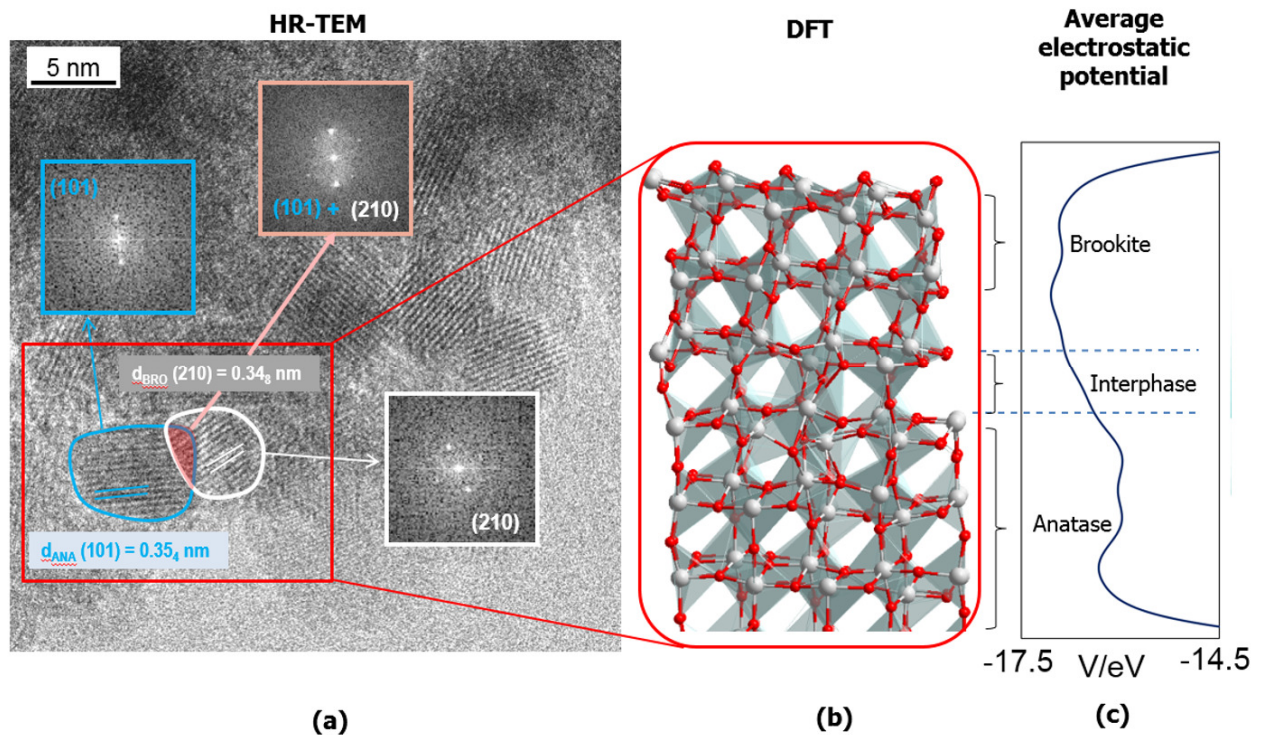


Figure 1. From nanoparticle imaging to circuit electrochemical modeling via first-principles atomistic calculations. (a) HR-TEM image of anatase:brookite 77:23 w/w nanopowders (Section S2 SI). The insets represent the electron diffraction patterns relative to the two nanoparticles evidenced in blue (anatase) and white (brookite), respectively. The third electron diffraction, indicated as “Interface”, refers to the overlapping region (evidenced in red) between the two above examined nanoparticles. The material is highly crystalline, with neatly visible interference fringes with periodicity of anatase (101) and brookite (210) crystallographic planes. Spheroidal crystallites have average estimated diameters of 4–8 nm and the two phases statistically dispersed in a

homogeneous mixture. (b) Atomistic model of the structure of the $\{101\}_{\text{anatase}}:\{210\}_{\text{brookite}}$ interphase, fully relaxed at the DFT+U/PBE level of theory (see Methods and Section S3 SI). Curly brackets indicate from above to below the brookite, the interphase and the anatase regions respectively. (c) Plane-averaged electrostatic potential (eV) for the mixed anatase/brookite system, as a function of the non-crystallographic Z coordinate, i.e. along the slab perpendicular. ~~(d) The resulting double layer behaves as a nano-heterojunction where a complex 3D network of solid-solid interphases is acting as intimately associated nanoscale capacitors with EIS-estimated specific charge transfer of $4.2 \mu\text{C}\cdot\text{cm}^{-2}$ (see Methods and Section S4 SI). The agreement with the DFT estimate $5.4 \mu\text{C}\cdot\text{cm}^{-2}$ is remarkable.~~

Accordingly, we simulated ~~have developed a quantum mechanical model of this~~ the (101):(210) contact at the DFT/PBE+U level of theory (full details in Methods and Section S3 SI). ~~The hybrid anatase/brookite supercell was built by conveniently matching the mesh of the (101) anatase surface with the (210) brookite one. Given the geometrical mismatch between these surfaces, an educated guess where the 1x1 surface mesh of brookite has been oriented to fit as much as possible the 2x1 one of anatase was constructed prior optimization (Section S3.3 and S3.4 SI).~~ The optimized atomic arrangement presents a ~ 1 nm thick interphase layer (Figure 1b), which is somewhat more reminiscent of the brookite bulk structure. This is confirmed by the rumpling curve reported in Section S3.4 (Figure 6 SI), where the averaged root-mean-square deviation (RMSD) of each atom position from the respective bulk one is reported. The anatase-like region recovers the original bulk arrangement after 1 nm from the contact region, while the brookite-like one after 0.4 nm. The slab dimensions are chosen large enough to describe all relevant rearrangements that are taking place at the interphase. The slab surface layer atoms in contact with the vacuum are kept frozen at the bulk geometry and they are under-coordinated. ~~In this way,~~ Thus, the interphase region ~~optimization~~ is immune from the surface-vacuum interactions and the optimization is driven ~~it depends only on~~ by the anatase and brookite original bulk configurations. ~~We verified that~~ The polarization effects induced by this choice ~~are compensating of~~ on both sides of the slab compensate each other. Thus, ~~they do and~~ not influencing the ~~interphase~~ charge distribution of the interphase layer, as it can be

appreciated from the plane-averaged electrostatic potential along the non-crystallographic direction (Figure 1c and Section S3.7 SI, Figure S11 SI).

Computed Charge Density and Electrochemical Impedance Spectroscopy measurements

Integration of the DFT ground-state charge density within the topological atomic basins defined according to the Quantum Theory of Atoms in Molecules⁴⁸⁻⁵⁰ estimates a net migrationtransfer of ~ 0.5 electrons from the anatase to the brookite side of the interface (See SectionFigure 1e and S3.6 SI). Atomic charges are reported in Tables 1 and 2 of SI, and in Fig.S10a using a color code. These are relatively constant throughout the slab ~~and there are not~~; no specific oxidizing or reducing centers can be found. Accordingly, we do not focus on individual atomic charges, whose calculation and interpretation are still an open issue.⁵¹ Rather, the overall charge migrationtransfer between the two phases corresponding to the electronic ground state, which involves an electronic rearrangement in the whole anatase and brookite structures, is much more informative, as it can be also accessed experimentally by Electrochemical Impedance Spectroscopy (EIS, Figure 2+). The systems were studied without the addition of any electrochemical probe, to evaluate only phenomena deriving from the electrode material, the supporting electrolyte and the inert solution. Moreover, all the measurements were carried out in the absence of UV excitation, i.e. in the dark, to probe just the ground-state macroscopic properties of the MPP nanopowder. The potential was set to 0 V (SCE), very close to the open circuit potential of the electrochemical cell, to avoid phenomena driven by potential changes. The behaviour of FTO is very similar to that of a pure capacitor (vertical line with a slope very close to 90°, confirmed also by the corresponding Bode plot in Figure 2b). Instead, the oxide samples deviate from the linear trend, as expected. In Figure 2b more evidences for an additional RC element in the Anatase/Brookite sample are reported. The anatase sample presents two peaks, ascribable to RC of the two interphases, corresponding to one

with the solution and the other with support. The mixed anatase:brookite sample is very similar to the pure anatase one (given the predominant presence of anatase), but a third peak is appreciable between 1 and 10 Hz, related to a new anatase and brookite contact (the third interphase).

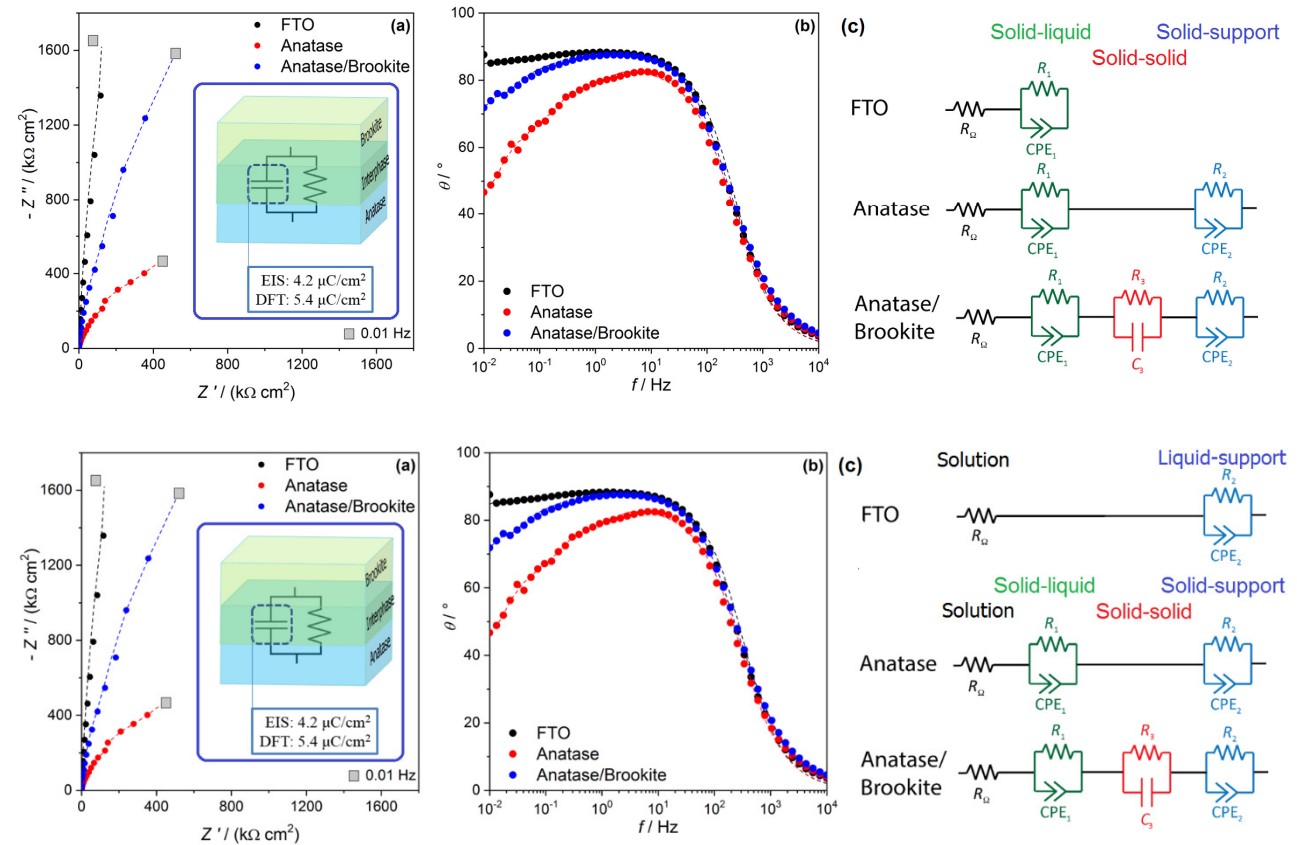


Figure 2. (a) Complex-plane plots in panel (a) and phase Bode plots in panel (b) for the following samples: pristine support (Fluorine-doped Tin Oxide, FTO, black dots), pure anatase (Alfa Aesar 284, fifth row in Table 1, red dots), and anatase/brookite mixed oxide (T400, seventh row in Table 1, blue dots). Dashed lines represent the fitting, performed with the equivalent circuits showed in panel (c) for the solid-liquid (green), solid-solid (red) and solid-support (light blue) interfaces. Fitted parameters are shown in Table 1. Inset of panel (a): The resulting double layer behaves as a nano-heterojunction where a complex 3D network of solid-solid interphases is acting as intimately associated nanoscale capacitors with EIS-estimated specific charge migration transfer of $4.2 \mu\text{C}\cdot\text{cm}^{-2}$ (see Methods and Section S4 SI). The agreement with the DFT estimate of $5.4 \mu\text{C}\cdot\text{cm}^{-2}$ is remarkable.

The experimental data were fitted (Figure 2b) using the equivalent circuits of one (FTO, support), two (pure anatase sample) and three (anatase/binerookite sample) RC series (Figure 2c). The results are summarized in Table 1. The capacitances at the interphases with the solution (CPE_1) and with

the support (CPE₂) are fitted by a constant phase element $CPE = [(C_i\omega)^\alpha]^{-1}$, considering the inhomogeneous surface of the oxide layers and the consequent non-ideal capacitor contact.

Table 1. Fitted parameters for the circuit elements modeled as in Figure 2c. *C*: capacitance; *R*: resistance; CPE: constant phase element; α : exponent in $CPE = [(C_i\omega)^\alpha]^{-1}$ (see text).

| Sample | $R_\Omega / (\Omega \text{ cm}^2)$ | $CPE_1 / (\mu\text{F cm}^{-2} \text{ s}^{\alpha-1})$ | α_1 | $R_1 / (\text{k}\Omega \text{ cm}^2)$ | $C_3 / (\mu\text{F cm}^{-2})$ | $R_3 / (\Omega \text{ cm}^2)$ | $CPE_2 / (\mu\text{F cm}^{-2} \text{ s}^{\alpha-1})$ | α_2 | $R_2 / (\text{M}\Omega \text{ cm}^2)$ |
|---------|------------------------------------|--|------------|---------------------------------------|-------------------------------|-------------------------------|--|------------|---------------------------------------|
| | Liquid | = | | | = | | Liquid-support interface | | |
| FTO | 70.8 | = | = | = | = | = | 8.2 | 0.98 | 35.0 |
| | Liquid | Solid-liquid interface | | | Solid-solid interface | | Solid-support interface | | |
| Anatase | 86.6 | 65.6 | 0.99 | 1.1 | = | = | 10.9 | 0.93 | 0.4 |
| Ana/Bro | 67.7 | 47.8 | 0.89 | 42.9 | 19.6 | 13.1 | 9.9 | 0.99 | 2.6 |

R_1 shows a typical value of oxide/solution interphase, while R_2 is greater, as expected from the oxide inhomogeneous layers contact with the support. In any case, the anatase/brookite sample can be satisfactorily fitted only using 3 distinct RC elements. From the comparison among the order of magnitude of the three equivalent resistors R_1 , R_2 and R_3 , we can observe that the resistance describing the anatase/brookite interphase (R_3) is from 3 to 6 orders of magnitude lower (Ω vs. $\text{M}\Omega$ and $\text{k}\Omega$) than those describing the contact between the oxides and the solution or the FTO support. This result can be explained with the very close contact, at the sub-nanometer scale, of the two phases, in agreement with the theoretical and HR-TEM outcomes. More specifically, DFT calculations have shown that the brookite phase can be interconnected to the anatase one by a network of bonds without loss of continuity. If we consider, for example, that in comparison the interactions of the nanoparticles with the solvent are typically not of this type, the resistor order of magnitude different finds its atomistic explanation on our modeling. It is also worth noting that this interphase can be fitted with a pure capacitor instead of a constant phase element, demonstrating that the separation of charges leads to an almost ideal double layer capacitor with a specific capacitance of $19.6 \mu\text{F} \cdot \text{cm}^{-2}$ (Table 1). This double layer originates from the volume-weighted

average of all the nanocapacitors that are associated to individual heterojunctions, which provide a high significance to the EIS estimate. DFT simulations predict a net charge migration of $5.4 \mu\text{C}\cdot\text{cm}^{-2}$ (Figure S10 SI and Figure 2a, inset) across the interface, in close quantitative agreement with the EIS outcome ($4.2 \mu\text{C}\cdot\text{cm}^{-2}$, figure 2 and Table 1). The conformity of views between such estimates is noteworthy, even though it might be partly traced back to some kind of error cancellation, including intrinsic limits of DFT, non-ideality of surfaces and finite-T kinetic effects. However, the overall agreement between the impedance experiments and theory confirms that a significant amount of nanoheterojunctions involves the most stable $\{101\}_{\text{Anatase}}$ and $\{210\}_{\text{Brookite}}$ crystallite facets, as shown also by the HR-TEM images in Figure 1a and Figure S1 SI (see above). This is expected, as nanoparticles have been grown under thermodynamic control (Section 1 SI). Eventually, an equilibrium double layer is formed ~~at the nanoscale~~ (Figure 2a, inset) only when both anatase and brookite are present in the nanostructured powder. DFT simulations suggest that ~~with the brookite (anatase) side is negative (positive) (see above) and the anatase one positive~~. We searched for confirmation of this charge sign in the experimental literature, since our impedance experiment cannot provide this information. Other simulations are not of any help. In fact, previous calculations, which are based on ~~A~~ standard DFT band-gap alignment and that we reproduced on Sections S3.2 and S3.5 SI, where the two phases are calculated separately, could not reproduce this representation (~~Sections S3.2 and S3.5 SI for the Tersoff's results~~), as there the Valence Band (VB) of brookite is higher in energy by a fraction of eV compared to anatase. However, literature EIS measurements³⁰ show that the brookite VB has a lower energy (i.e. a more positive reduction potential), even if for a small amount, in agreement with other experimental estimates (see Fig.6 of Ref.³⁰). This means that the anatase VB is bended at lower energies, the brookite one at higher energies, i.e., the brookite-like region can allocate extra electrons at the expenses of the anatase-like one. This VB offset can be directly compared with ~~our~~ the T = 0 K ground electronic state

calculations results ~~reported above~~, where a partial electron ~~migration~~~~transfer~~ is observed from anatase-like phase to the brookite-like one, with the consequent formation of a double charge layer. In conclusion, experimental and computational evidences agree that some ground state charge density flows into the brookite lattice, that is, this phase acts as a thermodynamic reducing agent in the anatase:brookite electrochemical pair.

~~This picture is further corroborated by inspecting at the DFT~~ ~~To corroborate this picture, we~~ ~~calculated the~~ plane-averaged electrostatic potential along the ~~non-crystallographic~~ direction, ~~perpendicular to the slab surfaces~~ ~~which was computed~~ by averaging the quantum expectation values of the potential from the electronic wavefunction (Section S3.7, Figure 1c). Two quasi-plateaus, each for each polymorph, are neatly visible, the brookite-like one being the most negative. As the averaged potential reflects the distribution of the total charge density, a slight excess of negative charges in the brookite-like region is confirmed. We stress that this is the $T = 0$ K ground state electronic picture and it does not ~~imply that a photo-excited electron would transfer with this direction or with the opposite~~ ~~on~~ ~~allow to infer the direction of the charge transfer upon~~ ~~photoexcitation, which is investigated experimentally in the next section.~~ ~~EIS experiments (Section S4 SI) have been carried out to investigate the circuital properties of nanostructured hetero-~~ ~~junctions. It was found that a specific parallel resistor-capacitor (RC) equivalent circuit (Figure 1d)~~ ~~must be added in the model to explain the observed experimental response (Figure S13 of SI) only~~ ~~in biphasic anatase-brookite samples. The associated resistance is 3-6 orders of magnitude lower~~ ~~than in the oxide/solution and oxide/support interphases (Table S3 of SI), due to intimacy and~~ ~~homogeneity of the anatase-brookite contact. The capacitor component is almost ideal and features~~ ~~a specific capacitance of $19.6 \mu\text{F}\cdot\text{cm}^{-2}$ (Table S3 SI).~~

~~It is worth noting that this double layer originates from the volume-weighted average of all the~~ ~~nanocapacitors that are associated to individual heterojunctions, which provide a high significance~~

to the EIS estimate. DFT simulations of the $\{101\}_{\text{Anatase}}\text{-}\{210\}_{\text{Brookite}}$ interface predict a net charge transfer of $-0.5 e^-$, or $5.4 \mu\text{C}\cdot\text{cm}^{-2}$ (Figure S10 SI and Figure 1c), in close quantitative agreement with the EIS outcome ($4.2 \mu\text{C}\cdot\text{cm}^{-2}$, figure 1d). The conformity of views between such estimates is good, even though it might be partly traced back to some kind of error cancellation, including intrinsic limits of DFT, non-ideality of surfaces and finite-T kinetic effects. The agreement between experiment and theory implies that a significant amount of nanoheterojunctions involves the most stable $\{101\}_{\text{Anatase}}$ and $\{210\}_{\text{Brookite}}$ crystallite facets, as shown by the HR-TEM images in Figure 1a and Figure S1 SI. This is expected, as nanoparticles have been grown under thermodynamic control (Section 1 SI).

Photocurrent measurements

It has been substantiated again and again that heterogeneous mixtures of TiO_2 polymorphs with a predominance of anatase generally show greater photocatalytic yields than one-phase TiO_2 (See Section S7 SI). Specifically, the photocatalytic visible-light performances of N-doped anatase are significantly enhanced in the presence of the brookite phase, even respect to the rutile one. This has been explained by invoking a lower recombination rate of charge carriers, which in turn has been attributed to band alignment effects, and a charge transfer across the phase boundaries. Now we want to see if for our composites, which we now know to be characterized by the presence of a polarized interphase, the generated e^-h^+ pair recombines significantly slower and by what extent. More specifically, we want to prove that it is the concomitant presence of the two polymorphs, and consequently of their interphase, to be correlated to responsible for the e^-h^+ recombination changes. In this regard, p Photocurrent experiments⁵² were performed under UV light (see Methods, Figure 3a and S13 SI). Pristine anatase and the anatase/brookite mixed samples behaved differently, as the

corresponding normalized j/j_0 decays required two different least-squares models to provide a satisfactory fitting. This likely indicates the presence of neatly distinguishable decay mechanisms. Usually, the calculation of the transient time constant τ , an estimate of the recombination time, is based on the linearization of the first order exponential decay which describes the first 15/25 seconds of irradiation by the following empirical law:^{52,53}

$$J(t) = J(0) + A_1 e^{-\frac{t}{\tau_1}} \quad (1)$$

In Eq. (1), A_1 is a pre-exponential factor and τ_1 the time constant. The anatase/brookite mixed samples conform with this model (Figure 3b and S14b SI), which correspond to one decay mechanism that takes place on a second-long timescale (Table 2). A more complex function is needed to model the pristine anatase data (Figure 3a and S14 SI). We found that a bi-exponential decay curve properly fits the pristine anatase data (Figures 3a and Figure S14b SI).

$$J(t) = J(0) + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (2)$$

As shown in Table 2, the first time interval 0–3 seconds is mainly described by an exponential decay characterized by a fast ($\tau_1 \sim 0.4$ s) and a slow ($\tau_2 \sim 4$ s) recombination processes, taking place on an ~~order one~~ of magnitude larger timescale. Interestingly, these estimates are comparable with those found in multilayer Cr-doped titania⁵² and much larger than those attributable to fast e^-h^+ recombination alone. Hence, in pure nano-anatase, two significant slowdown mechanisms are already active, ~~likely due to an extended interconnected network of 3D interphases~~.

Overall, the fitted coefficients of Eq. (1) imply, ~~the result of which showed~~ substantially longer e^-h^+ recombination times in composite MPP-N-doped TiO₂ nano-powders (Figure 3a**b**). ~~In contrast, in the composite anatase-brookite nanoparticles, a single exponential function with kinetic constants~~

close to τ_2 provides the most reasonable fit (Figure 3b and Section S5 SI). Thus We must conclude that the overall recombination mechanism is different in the biphasic samples, where either the fastest and most efficient recombination route is switched off, or else the slower path dominates. In either case, the effect is to enhance the current density j/j_0 by ~ 40 percent points with respect to pure anatase at $t > 10$ s (Figure 2a3a,b).

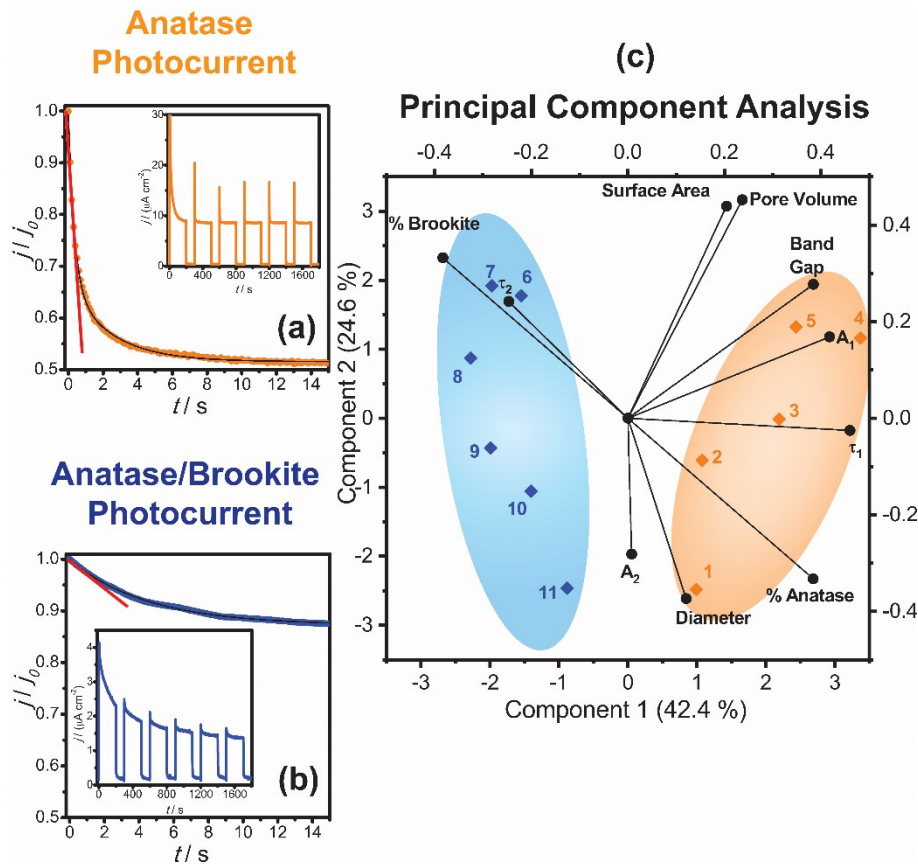


Figure 23. Slow-down of the e^-h^+ recombination time is correlated to the brookite phase presence. (a) Photocurrent measurements on commercial Alfa Aesar 130 anatase (see Table 2). Orange points: normalized j/j_0 current density decay for the first 15 s (4th step of irradiation). Measured data are shown in the inset. Black line: double exponential fit (parameters in Table 43 SI). Red line: first-order Taylor approximation of the exponential function close to $t=0$ s. (b) Same as (a), for the 96.4 anatase:brookite composite TiO_2 sample (blue points). A single exponential fit (black line) with lower $t \rightarrow 0$ slope (red line) accounts for these data. (c) Principal Component Analysis (PCA)-derived scores (black points) and loadings (black lines) for microstructural parameters of mono- (orange area) and bi-phasic (blue area) TiO_2 powders, showing their correlation with photocurrent estimates (original variables in Table 4-SI-2). A_1 and A_2 are fitted pre-exponential factors; τ_1 and τ_2 the corresponding recombination times ($\tau_1 \rightarrow 0$ for biphasic

samples, see Sections S5 and S6 SI). A strong positive correlation is apparent between the τ_2 kinetic constant and the brookite content.

~~As a further confirmation of the synergistic role played by the anatase/brookite mixing, photocurrent measurements were also performed on both mono- and bi-phasic TiO₂-based photocatalysts that differed by the w/w anatase/brookite ratio, the pore volume, and by the nominal concentration of the N dopant.~~

Table 2. Experimental data employed for the Principal Component Analysis study.

| Sample | N/Ti ^a | D ^b / nm | % A ^c | % B ^c | SA ^d / (m ² g ⁻¹) | V ^e / (mL g ⁻¹) | BG ^f / eV | τ_1 / s | τ_2 / s | $\frac{A_1}{\times 10^{-6}}$ | $\frac{A_2}{\times 10^{-6}}$ | Score ^g |
|--------------------------------|----------------------|---------------------|---------------------|--------------------|---|--|----------------------|-------------------------|----------------------|------------------------------|------------------------------|--------------------|
| Alfa Aesar 9.5 | 0 | 86 | 100 | 0 | 9 | 0.048 | 3.2 | 0.37 | 3.04 | 0.40 | 0.42 | 1 |
| Alfa Aesar 42 | 0 | 38 | 100 | 0 | 42 | 0.369 | 3.15 | 0.37 | 4.06 | 1.73 | 1.02 | 2 |
| Alfa Aesar 130 | 0 | 15 | 100 | 0 | 130 | 0.374 | 3.19 | 0.38 | 2.07 | 5.60 | 2.41 | 3 |
| Alfa Aesar 284 | 0 | 9 | 100 | 0 | 284 | 0.442 | 3.35 | 0.39 | 2.05 | 8.43 | 4.40 | 4 |
| Hombikat | 0 | 10 | 100 | 0 | 354 | 0.352 | 3.34 | 0.43 | 3.08 | 3.12 | 1.54 | 5 |
| T400 | 0 | 7 | 70 | 30 | 170 | 0.310 | 3.21 | 0.0001* | 3.08 | 0.0005* | 0.92 | 6 |
| TN_0.05 | 0.05 | 9 | 70 | 30 | 130 | 0.480 | 3.03 | 0.0003* | 4.80 | 0.0002* | 0.62 | 7 |
| TN_0.1 | 0.1 | 9 | 77 | 23 | 162 | 0.100 | 3.38 | 0.0002* | 5.09 | 0.0004* | 1.10 | 8 |
| TN_0.2 | 0.2 | 10 | 83 | 17 | 98 | 0.020 | 3.30 | 0.0001* | 4.03 | 0.0002* | 2.20 | 9 |
| TN_0.4 | 0.4 | 10 | 96 | 4 | 90 | 0.010 | 3.25 | 0.0002* | 4.07 | 0.0003* | 0.21 | 10 |
| TN_0.5 | 0.5 | 11 | 93 | 7 | 87 | 0.040 | 3.25 | 0.0003* | 1.04 | 0.0007* | 16.00 | 11 |

^a Nominal N/Ti molar ratio

^b Volume-averaged crystallite dimensions, as obtained from the Scherrer equation applied to the most intense (011) reflection of anatase (see Figure 15c SI).

^c Amount of anatase (A) and brookite (B) content, as estimated from fitting against the relative intensities provided by powder X-ray diffraction patterns (Figure 15c SI).

^d Specific surface Area (SA), as evaluated from BET-BJH analyses (Figure 15a SI).

^e Pore volume (V), as evaluated from BET-BJH analyses (Figure 15a SI).

^f Apparent band gap (BG), as derived from UV-vis diffuse reflectance spectra (DRS) (Figure 15b SI).

^g Score numbers in the PCA graph (Figure 3c)

* These values (three orders of magnitude lower than the measured values of the anatase pristine samples) are randomly assigned to avoid biases due to entries exactly equaling 0 in the PCA elaboration.

A Principal Component Analysis (PCA) of the main physical–chemical variables [listed in Table 2](#) (see also [Figure 3e and Section S6 SI Figure 3c](#)) shows that the decay time constant τ_2 correlates with the weight percent of brookite. In other words, *the phase composition, and not the amount of extrinsic point defects*, determines the [different \$e^-\$ – \$h^+\$ recombination mechanism and, therefore, the photocatalytic performances. As expected, higher time constants almost invariably correspond to higher photocatalytic efficiencies \(Section S5 SI\).](#) –The correlation [between \$\tau_2\$ and the brookite weight percent](#) is not linear, ~~however~~ though: the most brookite–rich powder (score n° [67](#)) has a higher decay rate ($\tau = 3.1$ s) than the EIS–analyzed 77:23 w/w specimen (score n° [78](#)), ~~whose~~ [where](#) $\tau = 5.1$ s [implies that it is the best performant photocatalytic material \(Figure S16 and Table S3 SI\).](#) Brookite–poor samples [89–110](#) all ~~show~~ [display](#) lower time constants ([Section S6 SI Table 2](#)) [and in fact are associated to lower conversion efficiency and smaller rate constants against the photodegradation of methylene blue, toluene and NO_x pollutants \(Figure S16 and Table S3 SI\).](#) Likely, they do not bear solid–solid interfaces large enough to produce a net ~~phase unbalance migration~~ [migration](#) of the charge carriers. ~~That said~~ [Moreover](#), [the](#) nanoparticle size might also influence the nature of the anatase:brookite double layer, and thus the decay rate. It has been shown that the band level alignment of anatase:rutile nanojunctions depends on quantum confinement effects:⁵⁴ the electron ~~migration~~ [transfer](#) at equilibrium might even switch from anatase → rutile to rutile → anatase upon increasing the dimensions of the nanoparticles in close contact. Whether and to what extent this is also true for anatase:brookite interphases remains to be investigated, and might disclose intriguing opportunities to design complex circuit elements at the nanoscale.

Conclusions

~~To summarize,~~ This contribution provides a first-principles atomistic description of biphasic TiO₂-based photocatalysts, revealing the formation of a 3D array of anatase-brookite nanodiode-like heterojunctions and correlating it to the enhanced visible-light photocatalytic behavior. In the first part of the paper, we focused on the ground state properties of the interphase nanocapacitor, finding a very good agreement among the hybrid supercell DFT modeling and the electrochemical impedance results. The hybrid supercell modeling presented herein, in combination with EIS and photocurrent electrochemical characterizations, paves the way towards the understanding of the electronic coupling between very small nanoparticles and of more complex and exotic confinement effects. ~~In the second part, we correlated photocurrent outcomes under UV illumination with several structural and compositional parameters, finding a significant, non-trivial correlation among the brookite content and the recombination time.~~ Our interpretative model, based on the atomistic details explaining the electronic interphase balancing, allows the generalization of 2D-heterojunctions to the more ubiquitous 3D case of coexistent crystalline nanoparticles of multi-phase polymorphs (MPP) photocatalysts ~~different phases. particular,~~ TiO₂-MPP devices have several advantages in the context of Green Chemistry applications: in particular, they are easily synthesizable from cheap reactants and environmentally safe. Moreover, crucial parameters like the polymorph ratio and the distribution of the dopant across the nanoparticle can be finely tuned by adjusting a few chemical and physical degrees of freedom ^{44,55-57}. Further research is needed to clarify the mechanism of e^-h^+ recombination delay in the excited states, but our preliminary ground-state results are encouraging and could disclose a new point of view for visible-light devices based on this architecture. ~~We think that in an effort to reach the ultimate goal of TiO₂ engineering, that is, to design photocatalysts with efficient sunlight performances~~ To this end, it is

~~necessary to understand~~ we stress the importance of investigating the physics of titania devices at atomistic scale. ~~Our results provide a self-standing picture of what is going on for nuclei and electrons in these devices in their ground state.~~ The recognition of the central role played by ~~the kind of~~ MPP nanoheterojunctions ~~that we have highlighted~~ could open new exciting scenarios for the tailored synthesis of TiO₂-based semiconductor photocatalysts with superior performances, paving the way toward an entirely novel class of cheap, easily synthesizable and environmental friendly composite materials. ~~We expect that devices based on the MPP heterojunction constructs may lead to important advances in Green Chemistry against contemporary societal challenges, as they bear huge application potential in Green Chemistry, and particularly in CO₂ reduction, wastewater treatment, sensors, energy transduction, and production of green fuels.~~

Experimental

Materials

Commercial single-phase TiO₂ powders have been purchased by Alfa Aesar (Anatase 9.5, 42, 130 and 284), Sigma-Aldrich (Brookite) and Sachtleben (Hombikat UV 100) and used without further treatments. Home-made powders, both undoped and N-doped, have been prepared by varying anatase/brookite quantity, following a previously optimized sol-gel synthesis.⁵⁷ Nominal N/Ti ratios of 0.05, 0.1, 0.2, 0.4 and 0.5 have been included.

HR-TEM

HR-TEM images were obtained by means of a JEOL 3010-UHR Instrument equipped with a LaB6 filament (acceleration potential 300 kV). All digital micrographs were acquired by an Ultrascan 1000 camera, and the images were processed by Gatan Digital Micrograph program version 3.11.1. Samples were dry dispersed onto Cu grids coated with “lacey” carbon film before the analysis.

DFT calculations.

[The computational procedure was originally developed by some of us \(LLP, MC, GDL\) at the Chemistry Dept. of Università degli Studi di Milano and then successfully applied to several other heterojunctions.](#)^{58–60} Simulations have been performed with VASP^{61–63} through a plane wave approach. Projector–augmented pseudopotentials, including spin–polarization, have been used in conjunction with the Perdew–Burke–Ernzerhof GGA parametrization⁶⁴ for the exchange–correlation functional. A Hubbard DFT+U splitting⁶⁵ has been considered and set to 3.0 eV for the Ti 3d states. The interface model has been built by exposing anatase (101) and brookite (210) surfaces of previously optimized pure phases, and then by putting them in close contact along the non–crystallographic direction as described in Section S3.3 SI. The final model consisted of a 3 nm thick anatase/brookite biphasic slab with 384 atoms, plus a 1.2 nm wide vacuum layer to separate translation–related images of the slab along the non–crystallographic direction. All atoms have been relaxed at constant volume of the simulation box, without imposing any symmetry constraint, with the only exception of the terminal layers in contact with vacuum, which have been kept fixed at their optimized bulk geometries.

Electrochemical Impedance Spectroscopy.

An electrochemical cell with Luggin capillary for ohmic drop abatement, a saturated calomel electrode for reference and electrode setup consisting in two Pt wire counter electrodes perpendicular to working and reference, has been used. The working electrode has been a fluorine–doped tin oxide (FTO) glass covered with a deposition of the desired sample. N₂–deaerated NaClO₄ 0.1 M has been employed as supporting electrolyte. Analyses are carried out by using a potentiostat/galvanostat PGStat30 (Autolab, The Netherlands) equipped with a FRA module and Nova 2.0 software.

Photocurrent and photocatalysis.

Photocurrent measurements performed with the same setup as EIS were registered at fixed potential of +1 V (step potential 0.1 s) under 500 W UV light irradiation (Jelosil HG 500, iron halides). The first 600 s represent the dark current, then 200 s of irradiation are alternated with 100 s at dark for 6 times. Photocatalysis experiments were performed using a 300W solar lamp emitting in the 380–600 nm range of wavelengths, with nominal intensity $I = 1.2 \times 10^{-5}$ Einstein $\text{dm}^{-3} \text{s}^{-1}$. Reagent-grade methylene blue, NO_x and toluene were the substrates examined.^{53,66}

Spectroscopic, BET and diffractometric characterization.

UV–vis spectra were recorded with a UV–vis scanning spectrophotometer (Perkin-Elmer, Lambda 35) equipped with a diffuse reflectance accessory. All spectra were acquired by working in reflectance mode and Kubelka–Munk elaboration is applied for the band gap evaluation. The BET surface area was determined by multipoint BET method using the adsorption data in the relative pressure (p/p_0) range of 0.05–0.3. Desorption isotherms were used to determine the pore size distribution using the Barret–Joyner–Halander (BJH) method with cylindrical pore size. XRD diffractograms are obtained with Philips PW 3710 Bragg–Brentano goniometer equipped with a scintillation counter and 1° divergence slit, 0.2 mm receiving slit, and 0.04° Söller slit systems. We employed graphite-monochromated Cu $K\alpha$ radiation at 40 kV \times 40 mA nominal X-rays power. Volume-averaged crystallite dimensions have been estimated through Scherrer equation on (101) anatase and (211) brookite reflections.

Supplementary Information

Supporting Information is available online or from the author.

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Conflict of interests

There are no conflicts to declare

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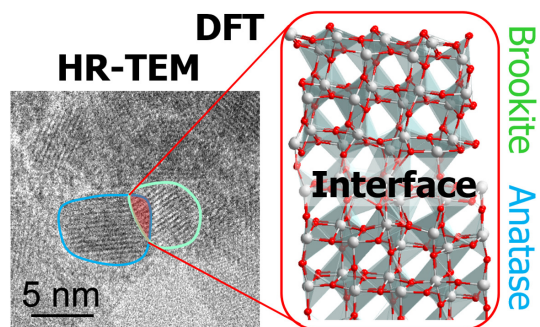
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Graphical Abstract



Description: A change of view for anatase/brookite 2D-heterojunctions into 3D patchworks of intimately associated mixed crystallites allows us to model the interphase as a nanocapacitor able to facilitate charge separation and photocatalysis.

Keywords: Computational chemistry, Density functional calculations, Electrochemistry, Interfaces, Nanoparticles