

Review Article

(Photo)electrochemical Methods for the Determination of the Band Edge Positions of TiO₂-Based Nanomaterials

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TiO₂-based nanomaterials play currently a major role in the development of novel photochemical systems and devices. One of the key parameters determining the photoactivity of TiO₂-based materials is the position of the band edges. Although its knowledge is an important prerequisite for understanding and optimizing the performance of photochemical systems, it has been often rather neglected in recent research, particularly in the field of heterogeneous photocatalysis. This paper provides a concise account of main methods for the determination of the position of the band edges, particularly those suitable for measurements on nanostructured materials. In the first part, a survey of key photophysical and photochemical concepts necessary for understanding the energetics at the semiconductor/solution interface is provided. This is followed by a detailed discussion of several electrochemical, photoelectrochemical, and spectroelectrochemical methods that can be applied for the determination of band edge positions in compact and nanocrystalline thin films, as well as in nanocrystalline powders.

1. Introduction

Although first scientific reports of photoinduced effects of titanium dioxide on chemical reactions were available already more than ninety years ago [1–8], it was first in the 1970s that potential practical applications of TiO₂ photoelectrochemistry and photocatalysis have been fully recognized. This was particularly due to the pioneering work of Fujishima and Honda on solar-driven water splitting into hydrogen and oxygen using a TiO₂ photoanode [9–11], which promised utilization of TiO₂-based materials for solar energy conversion and storage [12–16]. In following years further photochemical applications of TiO₂ have been realized, most of them motivated particularly by the advantageous combination of its low cost, nontoxicity, and excellent stability against photocorrosion. One important example is the rapidly growing field of heterogeneous photocatalysis [17–25], in which TiO₂ has been successfully employed in photooxidation reactions utilizing aerobic oxygen for the complete removal of pollutants from water and air [17–22, 24–39], in preparation of superhydrophilic and antifogging

surfaces [40–43], in photocatalytic organic syntheses [44–49], or in antitumor medicinal applications [50–54].

Importantly, although the bandgap energy of TiO₂ is rather large (for anatase 3.2 eV; ~ 390 nm) and direct band-to-band excitation can therefore only be achieved by high-energy UV light, the utilization of TiO₂ is not confined to UV-light-driven applications. Drawing on the fundamental studies on dye sensitization of other wide bandgap semiconductors (ZnO, SnO₂) in the 1960s [55–59], attaching visible-light-absorbing organic dyes to the surface of TiO₂ [60, 61] has led to fabrication of regenerative dye-sensitized solar cells with the overall solar conversion efficiencies exceeding 10% [62–64]. Other sensitization approaches utilize chromophores like semiconductor quantum dots [65–70], plasmonic metal nanocrystals [71–75], simple coordination compounds like chloroplatinate (IV) complexes [29, 32, 76] or ferrocyanide ions [77–79], stable polymeric compounds [38, 39, 80–83], or metal ions (Cu²⁺, Fe³⁺) grafted onto the TiO₂ surface [84, 85]. In contrast to these *surface*-confined sensitization protocols, *bulk*-doping of TiO₂ has also attracted significant interest. In the latter approach,

transition metals [86–88] or main-group elements like carbon [35, 89], nitrogen [31, 90–97], and sulfur [98, 99] are introduced into the lattice of titania resulting in formation of intrabandgap donor and acceptor levels, allowing thus for visible light ($\lambda > 400$ nm) excitation. Apart from the fields of solar cells and photocatalysis, the visible light-responsive TiO₂ materials opened up a route for further developments including photoelectrochemistry-based sensors [100, 101] and light-addressable photoelectrochemical optoelectronic devices [102–106].

Obviously, many applications can benefit from TiO₂ materials with fine-tuned structural and surface characteristics. Particularly nanostructured and mesoporous materials with a large surface-to-volume ratio are highly profitable for most applications. This motivated the development of a great variety of synthetic protocols which allow for fabrication of TiO₂ with well-defined morphologies on the micro- and nanoscale. These include, for example, nanoporous spheres [107], nanotubes [108, 109], hierarchical nanodendrite-nanoparticle composites [110], organized mesoporous TiO₂ films with controlled crystallinity [111, 112], nanoparticles with distinct crystal facets [113, 114], or TiO₂ inverse opals materials exhibiting photonic bandgap [115–117]. In addition, the modification of surface catalytic properties has been achieved, for instance, by coupling TiO₂ with gold nanostructures [118], graphene [119], or reduced graphene oxide [120, 121].

Notwithstanding the huge variety of different TiO₂-based materials, it is important to realize that the fundamental basis for all photochemical applications of TiO₂ is its *semiconducting* electronic structure [122, 125–129]. In other words, it is the energy band structure that underlies the photoactivity of TiO₂-based materials, whereby the position of the band edges on the electrochemical potential scale exerts a crucial influence on the operation of the photochemical system. This can be well exemplified in Figure 1. A typical photocatalytic reaction at small TiO₂ particles is initiated by absorption of a UV light photon, whereby a pair of charges is generated—an electron in the conduction band and a hole in the valence band (Figure 1(a)). The photogenerated charges can either recombine or undergo an interfacial electron transfer process, whereby the electron reduces an electron acceptor species A to a primary reduction product A^{•-}, and the hole oxidizes an electron donor species to D^{•+}. Hence, for example, during a typical photocatalytic oxidation of organic pollutants on TiO₂ in aqueous solutions, the reacting holes are scavenged either directly by the pollutant or by adsorbed hydroxyl ions to produced hydroxyl radicals which can then oxidize the pollutant due to their high oxidizing power. Simultaneously, the photogenerated electrons reduce molecular oxygen to a superoxide radical ($E_{O_2/O_2^{\bullet-}} = -0.16$ V versus NHE [130]) which can then undergo further reactions to produce hydroxyl radicals [17, 131–134]. It is obvious that the positions of the conduction and valence band edges are of crucial importance here since these give information on the reductive and oxidative power of photogenerated electrons and holes, respectively. Interestingly, the product of the one-hole oxidation of some electron donors—like, for example, the methoxy radical as a primary oxidation product

of methanol (Figure 1(b))—is a very strong reducing agent that can inject an electron into the conduction band of TiO₂ and is thereby further oxidized to formaldehyde. Since this generation of *two* electrons in the conduction band upon absorption of *one* photon has been first observed during photocurrent measurements, it has been coined as the *photocurrent-doubling effect* (photocurrent-multiplication effect) [125]. It goes without saying that the position of the conduction band edge on the potential scale will again play an essential role for the efficiency of the electron injection in such a case. Obviously, similar consideration will be also valid in cases when the photoprocess is based on light absorption by a sensitizer, typically a dye (Figure 1(c)). Here, the dye gets into an excited state from which it injects an electron into the conduction band of a semiconductor and is thereby oxidized. Alternatively to this *photoinduced electron transfer* scenario, in case of a strong coupling between the sensitizer and TiO₂ the so-called *direct optical electron transfer* from the chromophore's HOMO into the conduction band of TiO₂ can occur, as known, for example, for TiO₂ covalently sensitized with catechol [135–137], chlorophenols [138, 139], or polymeric compounds [140]. In case of TiO₂-assisted photooxidation reactions based on sensitization, one often speaks about “*indirect* photocatalysis” since the reaction is not initiated through direct photon absorption by TiO₂ (“*direct* photocatalysis”; Figure 1(a)), but instead indirectly, through the light absorption by a dye [24, 25, 34, 37]. At any rate, the position of the conduction band edge must be positive enough in order to allow for the injection from the dye, and at the same time negative enough, in order to allow for further electron transfer to suitable acceptors in the solution (e.g., oxygen).

From the above stated, it is clear that the positions of the band edges exert a crucial influence on the photoactivity of TiO₂-based materials. In this context, it is rather surprising that the determination of the band edge position is still only very rarely directly addressed experimentally, particularly in research directed to the development of new photocatalysts. This causes a serious lacuna in our understanding of the photoactivity of such novel materials since the position of the band edges in many cases cannot be simply predicted or taken from the literature data. This is due to the fact that the band edge positions of TiO₂-based materials will normally depend on surface charging. This will be highly dependent not only on the ionic conditions in a concrete electrolyte (pH, specific adsorption of ions), but also on the surface structure and composition of the material, which, in turn, will depend on the particular synthetic strategy used for the fabrication. The aim of this paper is to review various methods for the measurement of the band edge positions of TiO₂-based materials. The focus will be particularly on nanostructured materials used in photocatalysis and other applications operating in aqueous electrolytes. The paper will start with a short summary of some fundamental concepts of semiconductor photophysics and photochemistry (quasi-Fermi levels, flatband potential, pH dependence of band edges) that are directly relevant for understanding the problem of band edge determination. Then, a theoretical approach to the calculation of the band edges position, together with

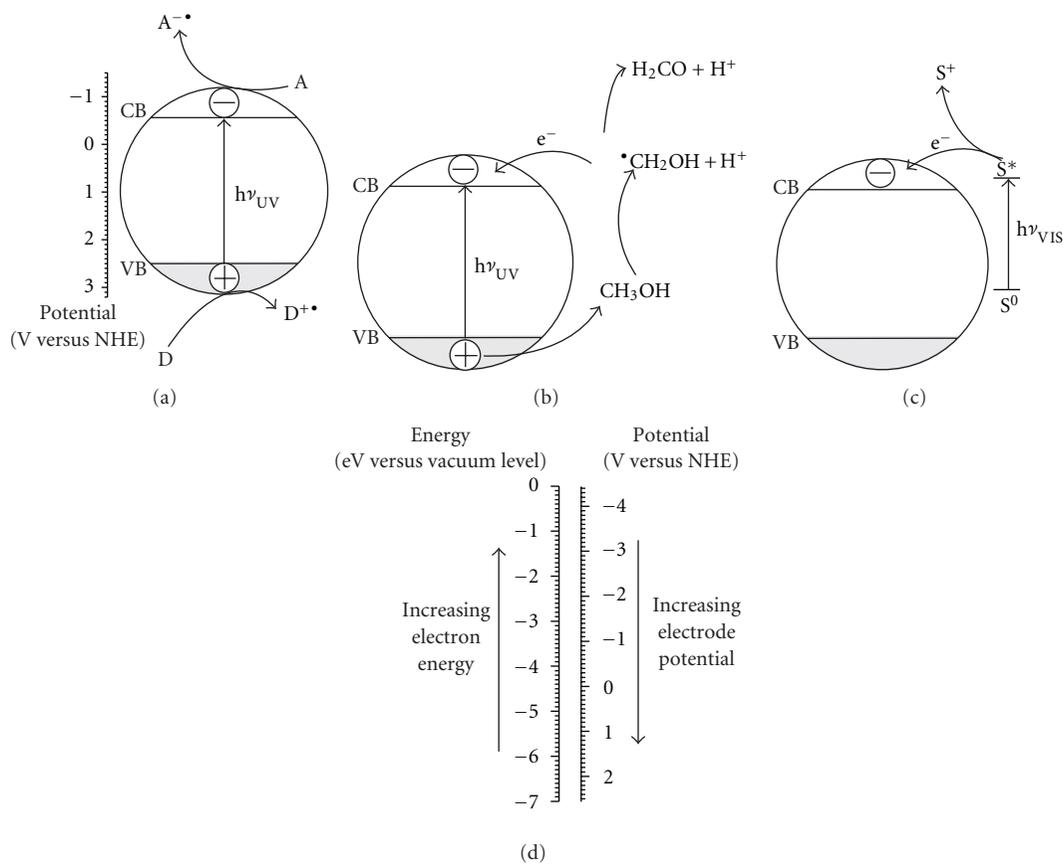


FIGURE 1: Schematic view of different TiO_2 -assisted photoprocesses. (a) Direct photocatalysis initiated by excitation of an electron from the valence band (VB) to the conduction band (CB) of TiO_2 . (b) Mechanism of “photocurrent multiplication” at an irradiated TiO_2 electrode in the presence of methanol. (c) Sensitization of TiO_2 by a dye: the dye is photoexcited with visible light from its ground state S^0 to excited state S^* , injects an electron to the conduction band of TiO_2 , and is thereby oxidized to S^+ . All recombination pathways are omitted for the sake of clarity. Whereas the common convention in solid state physics relates the positions of band edges with respect to the vacuum level, in photoelectrochemistry and photocatalysis, the potentials are usually given with respect to the normal hydrogen electrode (NHE; $E_{\text{NHE}} = 0 \text{ V}$). On the energy scale, the NHE is reported to lie at $-4.44 \pm 0.02 \text{ eV}$ (at 298.15 K) with respect to the vacuum level [122]; for more details, see [123, 124].

the application of conventional spectroscopic and contact potential difference measurements, will be shortly discussed. This will be followed by a detailed discussion of various electrochemical, photoelectrochemical, and spectroelectrochemical methods that can be applied to measurements on TiO_2 -based materials in the form of thin compact films, porous nanocrystalline layers, and nanocrystalline powders.

2. Theory and Fundamental Concepts

2.1. Quasi-Fermi Levels and Flatband Potential. TiO_2 is typically found in one of its three main crystal structures: rutile (tetragonal), anatase (tetragonal), or brookite (orthorhombic). Out of these, anatase is the polymorph most widely used for photocatalytic and photoelectrochemical purposes. It is noteworthy that the conduction band edge states have predominantly the Ti $3d$ character, while the valence-band edge states have the O $2p$ character. Importantly, due to its inherent nonstoichiometry (oxygen vacancies), TiO_2 is typically a rather heavily doped n-type semiconductor. This

means that its *Fermi level* (E_{F}) is typically right below the conduction band edge (E_{C}). From the thermodynamic point of view, the Fermi level is the electrochemical potential of the electron in the solid. Equivalently, from the statistical point of view, the Fermi level is the energy at which the probability of an energy level being occupied by an electron (the Fermi function) is 0.5 (Note, however, that this does not imply that the level at the Fermi energy is populated by electrons because the population depends upon the product of the Fermi function and the electron density of states). Hence, the Fermi level describes the occupation of energy levels in a semiconductor at thermodynamic equilibrium. However, the condition of thermodynamic equilibrium is not always fulfilled—particularly when excess electrons and holes are photogenerated under illumination or injected under electric bias. Accordingly, the electron and hole densities in the conduction and valence band are not described by the same Fermi level but by a *quasi-Fermi level* of electrons ($*E_{\text{Fn}}$) and a *quasi-Fermi level* of holes ($*E_{\text{Fp}}$), respectively (Figure 2) [125, 126, 128]. In general, the density of majority carriers

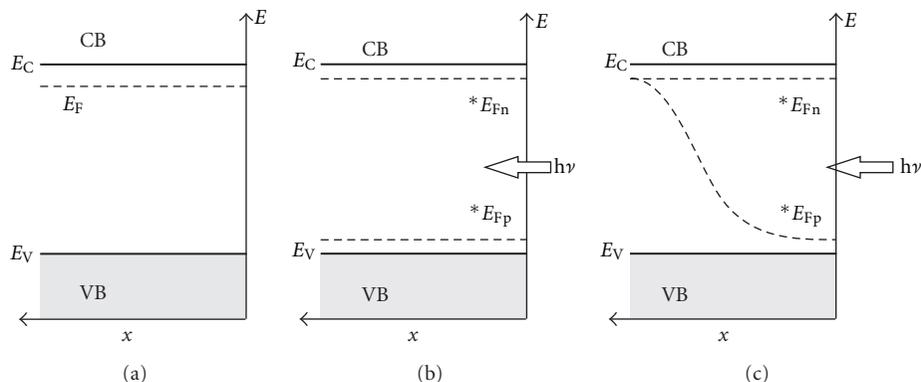


FIGURE 2: Fermi levels and quasi-Fermi levels of electrons and holes for an n-type semiconductor: (a) at thermodynamic equilibrium (in the dark); (b) and (c) under illumination; (c) local excitation; x is the distance from the semiconductor surface (adapted from [128]).

(electrons in case of TiO_2) does not significantly increase upon illumination and the quasi-Fermi level for majority carriers is normally almost the same as the Fermi level at equilibrium. In contrast, the density of minority carriers (holes) can be increased by many orders of magnitude, which then leads to a shift of the quasi-Fermi level of holes ($*E_{Fp}$) downwards to the vicinity of the valence band edge.

It should be also noted that the generation of electron-hole pairs often occurs locally near the semiconductor surface due to the small penetration depth of light, which leads to variations in the quasi-Fermi level of holes with the distance from the surface (Figure 2(c)). Importantly, in case of heavily doped n-type metal oxides like TiO_2 , the lower conduction band edge, E_C , practically merges with the quasi-Fermi level for electrons, $*E_{Fn}$, ($|E_C - *E_{Fn}| < 0.1 \text{ V}$) [125]. Therefore, as will be discussed below in more detail, the determination of the conduction band edge often translates into the measurement of the position of the quasi-Fermi level of electrons. Once this is known, the position of the valence band edge can be simply calculated by adding the value of bandgap energy, that is, typically determined by optical [128, 141–151] or photoelectrochemical methods [152–156].

Another important concept, particularly in case of compact flat TiO_2 films that behave similarly to single crystal semiconductors, is the *flatband potential*. First, let us consider the energetic situation at the n-type semiconductor/electrolyte interface before and after the contact of the two phases (Figure 3). After the contact of the semiconductor surface with the electrolyte, the thermodynamic equilibrium on both sides of the interface must be established [125–128, 157]. In other words, the Fermi level of the semiconductor E_F is adjusted to the Fermi level of the electrolyte $E_{F,\text{redox}}$. The latter can be considered nearly constant because the number of available states per unit energy in the solution typically far exceeds the number present in a semiconductor. This equilibration happens through electron transfer across the interface, which results in formation of the space-charge layer—also called the “depletion layer” since the surface region of the semiconductor is depleted of its majority carriers. It is important to realize that, in the case of an n-type semiconductor, this interfacial charge-transfer process produces an

excess of positive charges in the semiconductor (immobile charges of ionized donors) and an excess of negative charges in the electrolyte. With more electrons exchanged, the electric field of the negative charges on the solution side hinders further electron transfer so that the equilibrium is established in which no net charge flow occurs. As a consequence, the bands are bent upwards, which can be understood in terms of a continuously growing barrier for interfacial electron transfer when moving from the bulk of the semiconductor to the interface due to the continuously less efficient screening of the negative charges in the solution by the positive charges in the depletion layer [127]. The height of the barrier is the energy difference between the conduction band edge in the bulk (E_C) semiconductor and the conduction band edge at the surface ($E_{C,s}$) and corresponds to the potential drop in the space-charge layer U_S .

The charge distribution scenario at semiconductor/electrolyte interface is summarized in Figure 4. Importantly, three distinct double layers can be distinguished at the interface. First, it is the semiconductor space-charge layer with positive charges in the form of ionized donors and the counter negative charge located at the surface. The second one is the Helmholtz double layer consisting of the inner Helmholtz plane (IHP) and the outer Helmholtz plane (OHP). The first is located at the semiconductor surface, and the charge is in the surface states or at the location of specifically adsorbed ions, whereas the latter denotes the position of the closest approach of hydrated mobile ions. Finally, there is the Gouy-Chapman layer which is extended region with an excess of free ions of one sign. Essentially, the double layers act as parallel-plate capacitors connected in series with capacitances C_{SC} , C_H , and C_G representing the capacitance of the space-charge layer, the capacitance of the Helmholtz double layer, and the capacitance of the Gouy-Chapman layer, respectively, whereby C_G can be typically neglected for electrolytes containing relatively high concentrations of redox species (Figure 4(d)).

The simplest quantitative description of the situation at the semiconductor/electrolyte interface [125–129, 157] is analogous to the Schottky diode model and is based on the following assumptions: (i) ideal, crystalline semiconductor,

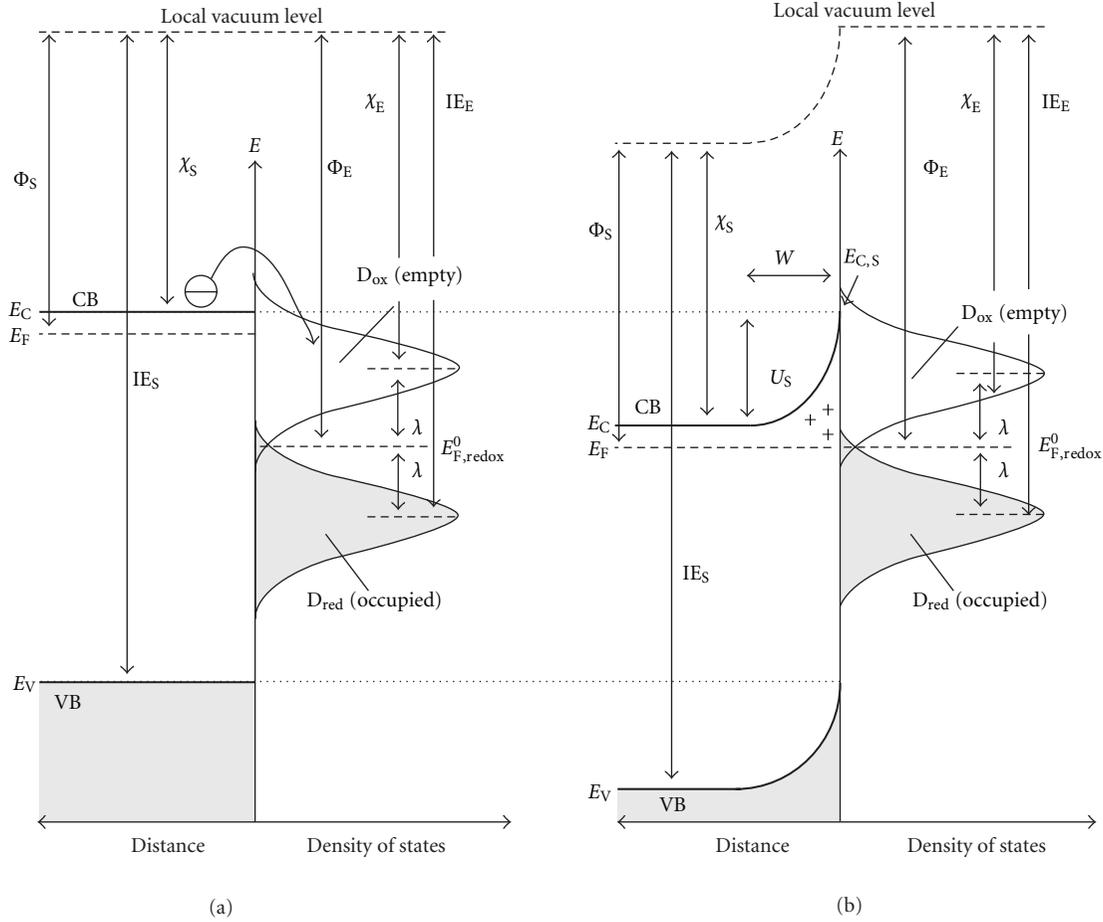


FIGURE 3: Schematic energy model of the n-type semiconductor/electrolyte interface before (a) and after (b) the establishment of equilibrium. The presence of surface states in the semiconductor is neglected. D_{red} and D_{ox} correspond to the distribution functions of the density of states for reduced and oxidized species, respectively, of the redox system (the energy distribution of reduced and oxidized species is different due to different solvation; λ is the reorganization energy). Φ , χ , and IE are the work function, electron affinity, and ionization energy, respectively, of the semiconductor (index S) and of the electrolyte (index E).

homogeneous donor level near the conduction band (oxygen vacancies in the form of Ti^{3+} sites in case of TiO_2) with all donors ionized (all the electrons from the Ti^{3+} donors have been thermally excited to the conduction band); (ii) no surface states; (iii) potential drop in the Helmholtz layer can be neglected. The potential and charge distribution within the space-charge layer can be then described by a one-dimensional Poisson equation:

$$\frac{\partial^2 \varphi}{\partial x^2} = -\frac{1}{\varepsilon \varepsilon_0} \rho, \quad (1)$$

where φ is potential, x is distance, ε and ε_0 are the relative permittivity of the semiconductor and the permittivity of vacuum, respectively, and ρ is the volume charge density. After two integrations assuming $\rho = qN$ (q is the elementary charge; N is the doping concentration) and the boundary conditions $d\varphi/dx = 0$ for $x = W$ and $\varphi = 0$ for $x = W$

(see [125, 126, 128] for details), one obtains the following relation for the width of the space-charge layer W :

$$W = \left| \frac{2\varepsilon\varepsilon_0}{qN} \left(U_S - \frac{kT}{q} \right) \right|^{1/2}, \quad (2)$$

where U_S is the potential drop in the space-charge layer which can be obtained as

$$U_S = E_{\text{appl}} - E_{\text{FB}} \quad (\text{with external polarization}) \quad (3)$$

or

$$U_S = E_{\text{F,redox}} - E_{\text{FB}} \quad (\text{without external polarization}), \quad (4)$$

where E_{appl} is externally applied potential and E_{FB} is the potential at which $U_S = 0$ and the bands in the semiconductor are “flat” (*flatband potential*). It is now clear that the value of E_{FB} is of fundamental significance since it gives a direct information on the position of the conduction band

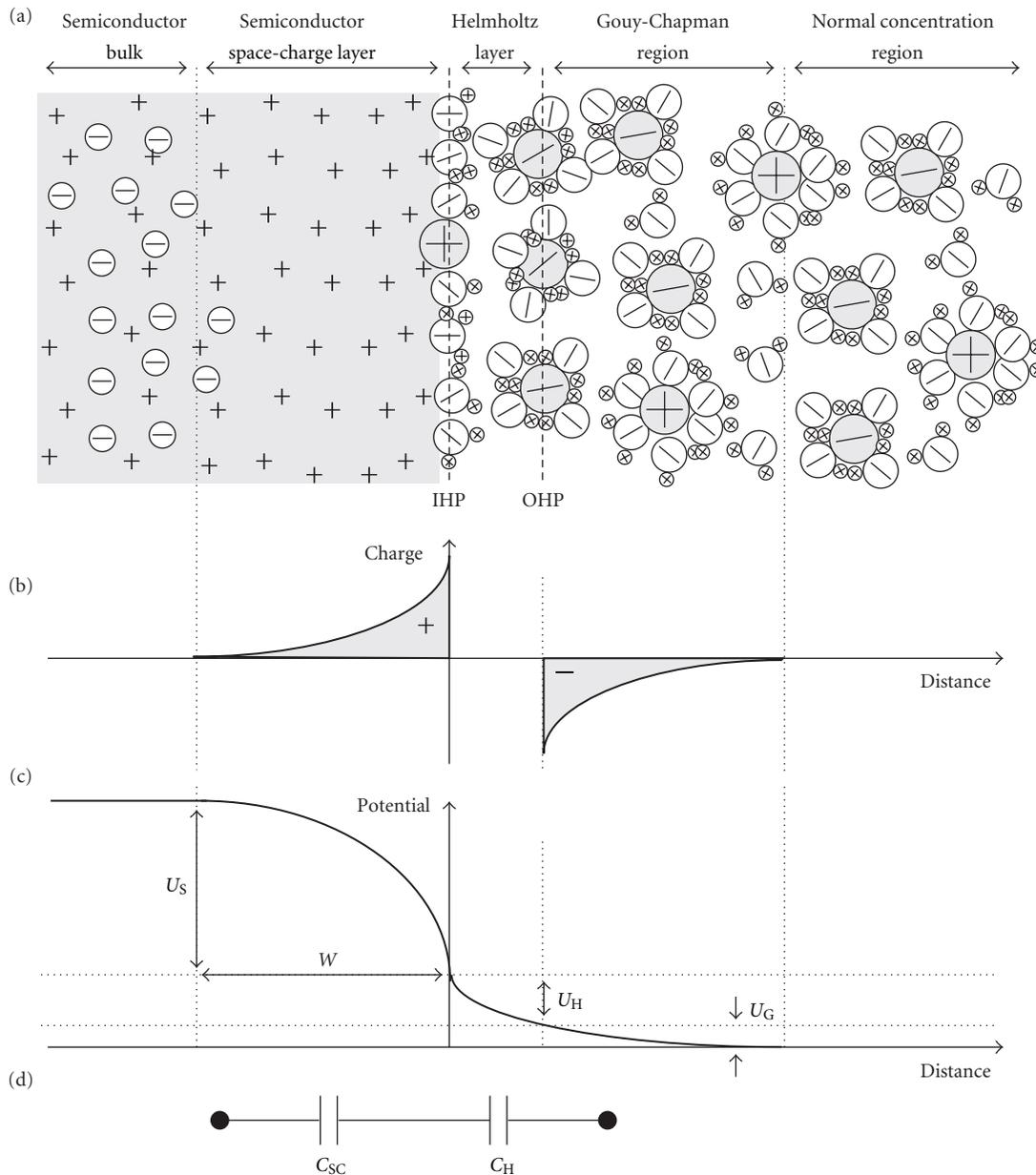


FIGURE 4: Schematic view of the electric double layers at the n-type semiconductor/aqueous electrolyte interface (a) with corresponding charge (b) and potential (b) distributions. U_s is the potential drop across the space-charge layer, U_H is the potential drop in the Helmholtz layer, and U_G represents the drop in the Gouy-Chapman layer; (d) the equivalent circuit for the interface assuming that U_G can be neglected.

edge at the n-type semiconductor's surface ($E_{C,S}$), assuming that the difference between E_{FB} and $E_{C,S}$ is very small for doped semiconductors. In other words, the determination of the conduction band edge of thin compact TiO_2 films often translates into the measurement of the flatband potential (for more details, see below). However, it should be emphasized that, in the context of nanomaterials, the above described formalism applies only to thin compact highly doped TiO_2 films that behave in a manner similar to compact crystalline semiconductors. In contrast, in small TiO_2 particles and in highly porous nanocrystalline electrodes, the formation of the space-charge layer is improbable due to the very

small crystallite size [158–163]. In other words, the nearly depleted small TiO_2 crystals do not contain enough electrons in order to create an effective space-charge layer. Several methods suitable for the determination of band edges in such nanocrystalline systems will be presented below.

2.2. pH Dependence of the Position of Band Edges. The position of the band edges at the surface ($E_{C,S}$) is determined by the charge at the surface, that is, by the potential drop in the Helmholtz layer U_H :

$$E_{C,S} = E_{C,S}^0 - qU_H, \quad (5)$$

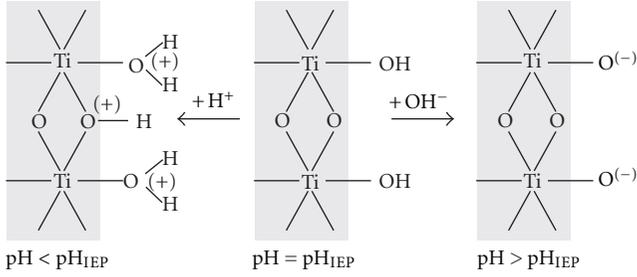


FIGURE 5: Simplified scheme of the protonation and deprotonation of hydroxylated TiO_2 surface leading to positive and negative net charge at the surface, respectively. The isoelectric point (pH_{IEP}) of TiO_2 is typically ca. 5.8–7.5 [125, 164–167]. The pK_{A} values of monodentate and bidentate OH groups are reported to be 12.7 and 2.9, respectively [166].

where $E_{\text{C,S}}^0$ is the position (on the energy scale) of the conduction band edge at the surface at $U_{\text{H}} = 0$. The Helmholtz double layer at semiconductors is typically determined through adsorption and desorption processes, which is particularly true for ionic oxide semiconductors like TiO_2 in aqueous electrolytes. In this case, the protons and hydroxyl groups play an essential role while the specific adsorption of other ions can be in most cases neglected.

In essence, the lattice Ti atoms act as Lewis acid sites and make the adsorption of hydroxyl ions possible, whereas the bridging lattice oxygen attracts protons and acts thereby as a Lewis base site. Hence, depending on the pH, the semiconductor surface becomes charged either positively or negatively (Figure 5). The pH value at which the net surface charge is zero is called the isoelectric point (pH_{IEP}) or the point of zero zeta potential (pzzp). (Here, it should be noted that pH_{IEP} and pzzp are *not* necessarily identical with the point of zero charge, pzc, that denotes the pH value at which H^+ and OH^- are adsorbed in equal amounts; when other ions than H^+ and OH^- are present and influence the charging of the surface, the pzc and the pH_{IEP} are not equal). The pH dependence of the conduction band edge at the surface can be then derived as follows [125]. Assuming $\text{pH} < \text{pH}_{\text{IEP}}$, we obtain the following equilibrium reaction:



where H_3O^+ is a hydroxonium ion in the solution and H_5O^+ is an adsorbed proton. The equilibrium is described by

$$\frac{[\text{H}_5\text{O}^+]}{[\text{H}_3\text{O}^+]} = \exp\left(-\frac{\Delta G}{kT}\right) = A \exp\left(\frac{-qU_{\text{H}}}{kT}\right), \quad (7)$$

where ΔG is the free Gibbs energy, U_{H} is the potential drop in the Helmholtz double layer, and A is a constant (assuming that ΔG varies linearly with U_{H}). Assuming $[\text{H}_3\text{O}^+] \gg [\text{H}_5\text{O}^+]$, the following relation can be obtained:

$$qU_{\text{H}} = B + kT \ln[\text{H}_3\text{O}^+] = B - 2.3kT \text{pH}, \quad (8)$$

in which $B = 2.3kT (\text{pH}_{\text{IEP}})$ assuming $U_{\text{H}} = 0$ at pH_{IEP} . By combining (5) and (8), we obtain now

$$E_{\text{C,S}} = E_{\text{C,S}}^0 + 2.3kT (\text{pH} - \text{pH}_{\text{IEP}}). \quad (9)$$

Accordingly, with increasing pH, the band edges at the surface shift to higher energies (on the energy scale), that is, to more cathodic potentials (on the electrode potential scale), whereby the shift at 298 K is typically $\sim 0.059 \text{ V/pH}$ unit.

2.3. Non-Ideal Behavior due to Surface States. The theoretical considerations described in Sections 2.1 and 2.2 assume that the charging of the semiconductor surface (i.e., the position of its band edges) is independent of the applied potential (applied bias voltage is effectively “consumed” within the space-charge layer) or irradiation (minority charge carriers are efficiently scavenged by species in the electrolyte). However, many semiconductors can have localized surface energy levels in the bandgap—the so-called “surface states”—which are typically related to crystal defects or surface damage, or they may result from surface reactions occurring in the dark or under illumination [128, 168, 169]. Obviously, relatively high density of surface states can be present at the surface of doped or surface-modified TiO_2 -based materials. It is important to realize that the presence of surface states can have significant effects on the position of band edges. During electrode polarization, the Fermi level can match the energy level of the surface states, which will lead to their charging. This might result in the change of the net charge at the surface (i.e., change in the potential drop across the Helmholtz layer), which will cause a shift of the band edge positions. Similarly, during irradiation, the surface states may act as traps for photogenerated charge carriers. Thus, for example, the minority charge carriers (holes in case of n-type TiO_2) or charged surface intermediates can accumulate at the surface, which will again lead to changes in the surface charging and result in “unpinning” of band edges [170]. In photoelectrochemical experiments, these problems can be to some extent avoided by adding efficient scavengers of minority charge carriers into the electrolyte [171].

2.4. Theoretical Predictions of the Position of Band Edges. Butler and Ginley introduced a theoretical approach for the prediction of the position of band edges using the following relation [125, 164]:

$$E_{\text{C,S}}^0 = E^c - X + \frac{1}{2}E_{\text{g}}, \quad (10)$$

where E^c is the energy of free electrons on the hydrogen scale ($4.44 \pm 0.02 \text{ eV}$), E_{g} is the bandgap energy, and X is the Sanderson electronegativity of the semiconductor, expressed as the geometric mean of the electronegativities of the constituent atoms, which are defined after Mulliken as the arithmetic mean of the atomic electron affinity and the first ionization energy (both in eV). Calculation for TiO_2 gives $X = 5.8 \text{ eV}$, which (assuming $(1/2)E_{\text{g}} = 1.6 \text{ eV}$ for anatase) yields the value of $E_{\text{C,S}}^0$ of $+0.24 \text{ eV}$ (relative to standard hydrogen electrode on the energy scale, i.e., -0.24 V versus NHE on the electrode potential scale). Interestingly, this result is only by $\sim 0.1 \text{ V}$ more negative than experimental results obtained by measurements on anatase single crystals [172]. Although several more sophisticated theories based on DFT calculations have been developed recently [173–175], the theoretical predictions cannot be always expected

to yield sufficiently reliable results, mainly in case of doped and surface-modified TiO₂-based materials.

2.5. Spectroscopic and Contact Potential Difference Techniques.

Obviously, some key quantities related to the positions of energy bands (see Figure 3) can be obtained also from spectroscopic and contact potential difference measurements performed in a “dry” (or “semidry”) state. Thus, for example, the ionization energy of the semiconductor (IE_S , defined as the energy needed to excite an electron from the valence band edge at the surface to the local vacuum level) can be measured by photoemission spectroscopy (e.g., UPS) [176]. On the other hand, the Kelvin probe method can be used for determination of the contact potential difference (CPD), that is, of the difference between the work function of a semiconductor and the work function of the metal tip of the probe (with known position on the energy vacuum scale) [177]. Moreover, the latter technique can be combined with illumination in the so-called surface photovoltage spectroscopy in which the changes of the CPD (i.e., of surface voltage) upon illumination are measured [178, 179]. Importantly, the saturation surface photovoltage is then directly related to the difference of the position of the Fermi level in the dark and the position of the *quasi*-Fermi level under illumination [180]. As an alternative to the Kelvin probe technique, the surface photovoltage can be also measured directly utilizing a metal-insulator-semiconductor structure and using chopped illumination in conjunction with lock-in detection of the surface photovoltage signal [178, 179]. Importantly in the context of this paper, a standard surface photovoltage measurement can typically be performed also in the presence of adsorbents like water molecules at the surface of the semiconductor (“semidry” state) [181]. Moreover, the Kelvin probe measurements of photoelectrodes immersed into electrolyte have been reported, whereby the electrode and the electrolyte were separated from the Kelvin probe tip by a very thin glass plate [182]. This method has been, for example, used for the estimation of the quasi-Fermi level in the TiO₂ nanocrystalline layers of dye-sensitized solar cells [183].

A more detailed discussion of these approaches is beyond the scope of this paper. Herein, we deal mainly with TiO₂-based materials for use in photocatalysis and photoelectrochemistry and the focus is on electrochemical and photoelectrochemical methods addressing the band energetics directly under operational conditions in (mostly aqueous) solutions. As already mentioned, experimentally the problem of determination of the band edge position is typically addressed by the measurement of the flatband potential or of the quasi-Fermi level. Several electrochemical, photoelectrochemical, and spectroelectrochemical methods will be now discussed in more detail.

3. (Photo)electrochemical Methods

3.1. Capacitance Measurements on Thin Compact Films. As already noted above, since thin compact TiO₂ films (e.g., dense anodic TiO₂ films on Ti) behave similarly to conventional macroscopic semiconductor electrodes, the Schottky

formalism can be applied and their conduction band edge potential can be measured as the flatband potential. Using the model of a parallel-plate capacitor, the Mott-Schottky relation can be obtained from (2):

$$\frac{1}{C_{SC}^2} = \frac{2}{\epsilon\epsilon_0qN_D} \left(E_{\text{appl}} - E_{\text{FB}} - \frac{kT}{q} \right). \quad (11)$$

The interface double layer capacitances C_{SC} and C_H can be treated as two capacitors connected in series (Figure 4(d)). The overall capacitance C is then given by

$$\frac{1}{C} = \frac{1}{C_{SC}} + \frac{1}{C_H}. \quad (12)$$

Under some conditions (a single crystal-like behavior, moderate doping, surface states neglected), it can be assumed that the width of the space-charge layer is much larger than the width of the Helmholtz layer, which yields $C_{SC} \ll C_H$ and, accordingly, $C \cong C_{SC}$.

A widely used technique for the determination of the capacitance is the measurement of impedance. In these experiments, an *ac*-voltage signal of small amplitude is used for the perturbation of the sample. From the current response, the impedance value and the phase shift can be determined. There are essentially two common impedance techniques, which enable us to get information about the capacitive behavior of a system. Either the impedance spectrum for a certain range of frequencies is measured (usually under potentiostatic conditions) or one particular frequency is chosen and the impedance is measured at constant frequency in dependence on the applied potential. Using the latter technique, the capacitance of the space-charge layer can be calculated from the imaginary part of measured impedance:

$$C_{sc} = \frac{-i}{2\pi f Z_{im}}, \quad (13)$$

where Z_{im} denotes the imaginary part of impedance, i is imaginary unit, and f is the frequency of *ac*-voltage signal. For determination of C_{sc} , a relatively high frequency is usually chosen and a simple equivalent circuit (neglecting the capacitive contribution of other elements) is employed for the interpretation of measured data.

From the resulting Mott-Schottky plot (C_{SC}^{-2} versus E ; see Figure 6), the flatband potential E_{FB} and the doping density N_D can be now obtained as the intercept with the x -axis and from the slope of the linear part. The value of the flatband potential from capacitance measurements on single-crystal anatase is reported to be -0.16 V versus NHE (pH 0) with a Nernstian behavior exhibiting a shift of -0.06 V/pH unit [172]. However, it should be noted that the impedance response of the probed system often contains all contributions of the experimental setup, including back contact capacitance, sample resistance, electrolyte resistance, capacitance and resistance of Helmholtz layer and of surface states, which sometimes causes non-ideal behavior and makes it difficult to obtain reliable values of E_{FB} (see Figure 6) when using highly simplified equivalent circuits as in Figure 4(d).

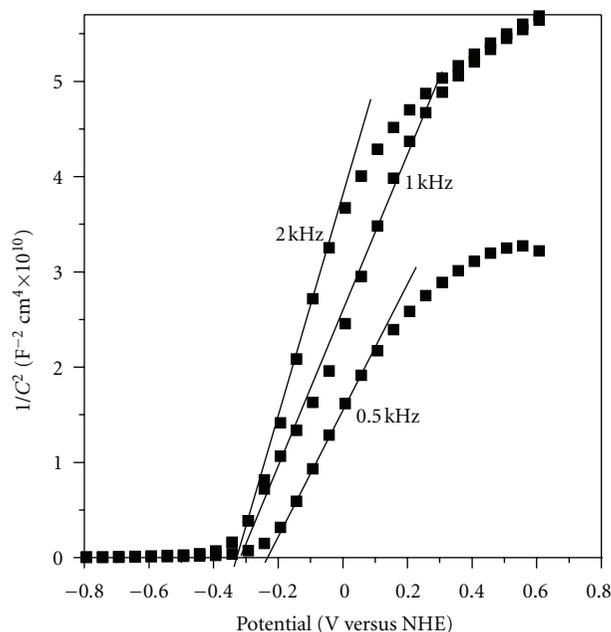


FIGURE 6: Mott-Schottky plots measured in a LiClO_4 (0.1 M; pH 6) electrolyte at three different frequencies on compact anodic TiO_2 layers. The frequency dispersion is a frequent phenomenon related to the nonideality of the semiconductor.

3.2. Photocurrent Onset Measurements. Another common method for the determination of the position of the conduction band edge is a measurement of the potential dependence of photocurrent. The principle of photocurrent generation is explained in Figure 7. If a compact n-type semiconductor (like, e.g., a dense anodic TiO_2 film on Ti) immersed in the electrolyte under depletion conditions is irradiated with light of higher energy than that of its bandgap, electron-hole pairs are generated and separated in the potential gradient of the space-charge layer (Figure 7(a)). In the case of an n-type semiconductor, this potential gradient drives photogenerated holes toward the semiconductor/electrolyte interface and electrons toward the interior of the electrode and from there to the electrical connection to the external circuit. Accordingly, anodic (positive) photocurrents are typically observed at TiO_2 photoelectrodes. Obviously, if we sweep the potential of the photoelectrode in cathodic direction (upwards on the potential scale), the band bending will be less and less pronounced. The diminished potential gradient and thickness of the space-charge layer will lead to enhanced recombination of photogenerated charges, which will, in turn, lead to constant decrease of photocurrents during the cathodic potential sweep. Finally, at the flatband potential, the photocurrent should disappear totally [184]. Hence, this so-called “photocurrent onset” potential can be considered to coincide with the flatband potential and to merge practically with the conduction band edge.

Interestingly, similar principle applies also in case of nanocrystalline porous electrodes, in which the photogenerated charge separation is not controlled by the potential gradient over the space-charge region since the crystallite size is too small to support an effective depletion layer [158, 159].

Here, the photocurrent is determined by the efficiency of photogenerated electron/hole transfer at the semiconductor/electrolyte and semiconductor/substrate interface [160–163]. This is schematically illustrated in Figure 7(b) which shows the mechanism of photocurrent generation at TiO_2 particles deposited on the conductive glass substrate (e.g., ITO). Assuming the presence of suitable redox species in the electrolyte, photogenerated holes immediately react with these at the surface of the particles. The photogenerated electrons can be transferred to the underlying conductive glass substrate, assuming that the Fermi level of the conductive glass is positive enough. Hence again, by moving the Fermi level of the ITO electrode cathodically, we should observe the disappearance of photocurrents when the potential of the underlying electrode (the Fermi level of ITO) reaches the quasi-Fermi level of TiO_2 particles, that is, their conduction band edge. In order to avoid scavenging of photogenerated electrons by oxygen dissolved in the solution, the electrolyte should be deaerated by purging with an inert gas prior to the measurement. Figure 7(c) shows a typical photovoltammogram recorded under interrupted illumination on a dense compact TiO_2 electrode during the cathodic sweep. It should be noted that the absolute values of E_C obtained are sometimes anodically shifted since the recombination becomes practically complete already at potentials relatively far (0.1–0.3 V) from the conduction band edge. Nevertheless, this method provides valuable information on shifts of E_C , particularly when a direct comparison can be drawn from measurements on different samples under otherwise identical conditions.

3.3. Open-Circuit Photovoltage Measurements. Apart from the capacitance measurements and the photocurrent onset determination, the value of E_{FB} can be also determined from the dependence of the electrode open-circuit potential (E_{OC}) on the illumination intensity (Figure 8). Under open-circuit conditions, the photogenerated holes can accumulate at the surface, which with increasing light intensity lowers the barrier U_S (see Figure 3) for electrons until the electrons can reach the surface at the same rate as holes. At the same time, the quasi-Fermi level (measured as E_{OC}) rises because of the higher occupancy of the conduction band. Accordingly, at sufficiently high-intensity, E_{OC} becomes constant and this value is very close to the potential of the conduction band edge [80, 125, 185–187]. In order to avoid reaction of photogenerated electrons with oxygen in the electrolyte, which would decrease the photovoltage, it is necessary to purge the solution with inert gas.

Figures 9(a), 9(b), and 9(c) show E_{OC} versus relative light intensity plots measured for a compact TiO_2 film at different pH values. It is seen that E_{OC} becomes independent of intensity when the latter exceeds relative values of 90%. The E_{FB} values plotted in Figure 9(d) show a nearly Nernstian linear dependence on pH with $E_{FB} = (-0.17 \pm 0.02) - 0.054(\text{pH})$ V versus NHE, in agreement with values reported for anatase TiO_2 [172]. Interestingly, the open-circuit photovoltage method yields reliable results also in case of nanocrystalline photoelectrodes [188, 189]. Under high-intensity illumination, the electrons accumulating in the conduction band and

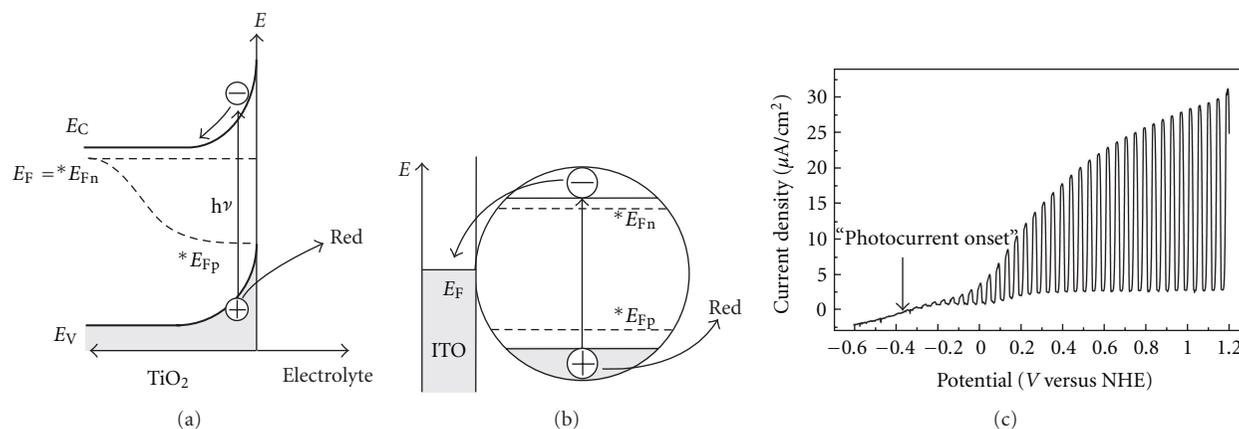


FIGURE 7: Schematic representation of the mechanism of photocurrent generation at a compact (a) and nanocrystalline (b) TiO₂ electrode. (c) Photovoltammogram under interrupted illumination for a compact TiO₂ electrode (dense anodic layer) recorded in LiClO₄ (0.1 M; pH 6) electrolyte in the cathodic direction with the sweep rate of 2 mV/s. The incident light wavelength was 350 nm.

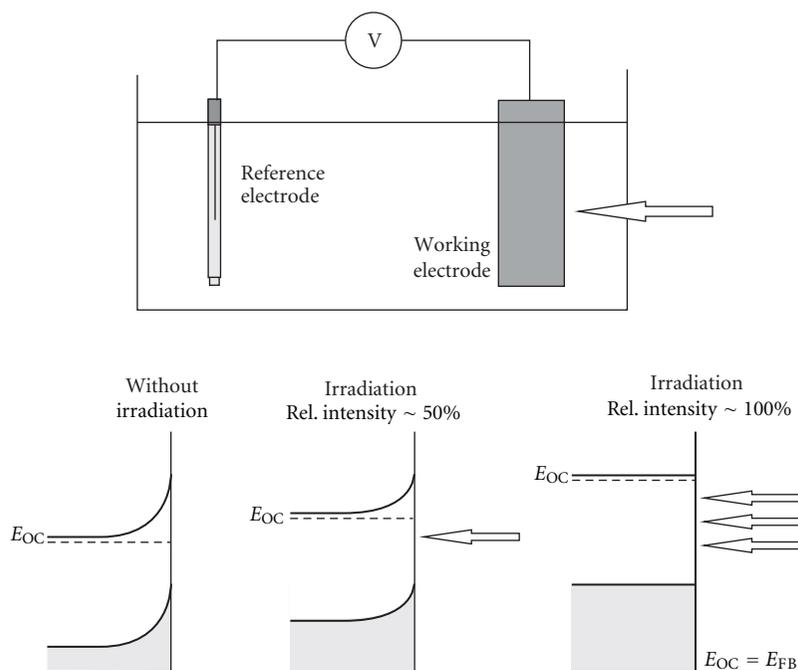


FIGURE 8: Schematic view of the flatband potential determination as the limiting value of the open-circuit potential (E_{OC}) under high relative irradiation intensity.

traps right below the conduction band edge cause the Fermi level of the conductive glass substrate to shift to the vicinity of E_C of TiO₂. It is again emphasized that intense purging with inert gas is absolutely necessary in order to avoid scavenging of photogenerated electrons by oxygen dissolved in solution.

3.4. Spectroelectrochemical Measurements on Transparent Films. The fact that many nanocrystalline films are *transparent* offers the possibility to determine the position of the conduction band edges using the spectroelectrochemical method of Fitzmaurice et al. [190–192]. The principle of

this method is schematically depicted in Figure 10. The Fermi level of ITO, E_F (ITO), can be controlled by applied potential, whereas the position of the conduction band edge of the transparent nanocrystalline TiO₂, E_C (TiO₂), depends only on the pH of the solution. At a constant pH, applying potentials more negative than E_C (TiO₂) leads to injection of electrons from ITO into the conduction band of TiO₂ (Figure 10(b)). During injection of electrons into the conduction band, the TiO₂ nanoparticles are not at thermodynamic equilibrium anymore; the Fermi level of TiO₂ is therefore properly designated as a *quasi-Fermi level*, $*E_{FP}$, and practically merges with the conduction band edge, E_C .

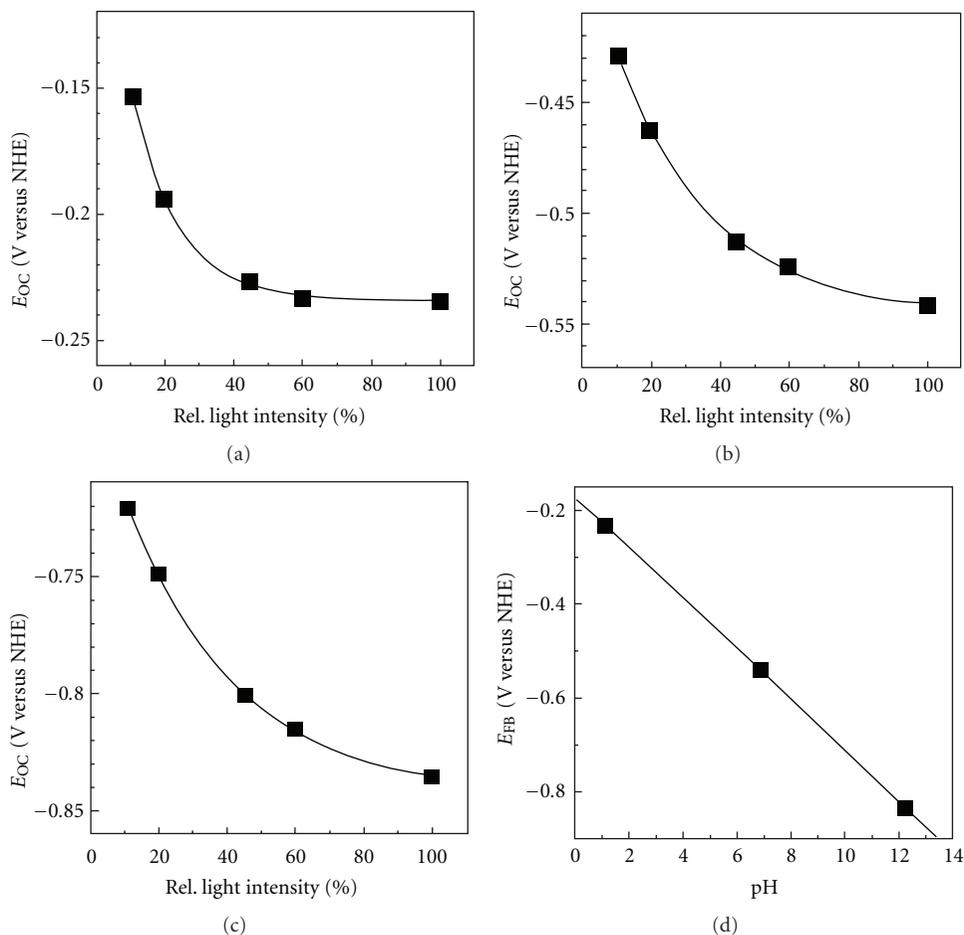


FIGURE 9: Dependence of the open-circuit potential (E_{OC}) on illumination intensity measured in (a) HCl (0.1 M; pH = 1.1), (b) NaCl (0.1 M; pH = 6.9), and (c) NaOH (0.1 M; pH = 12.3). (d) pH dependence of flatband potential (E_{FB}). The electrolyte was degassed by intense bubbling with nitrogen.

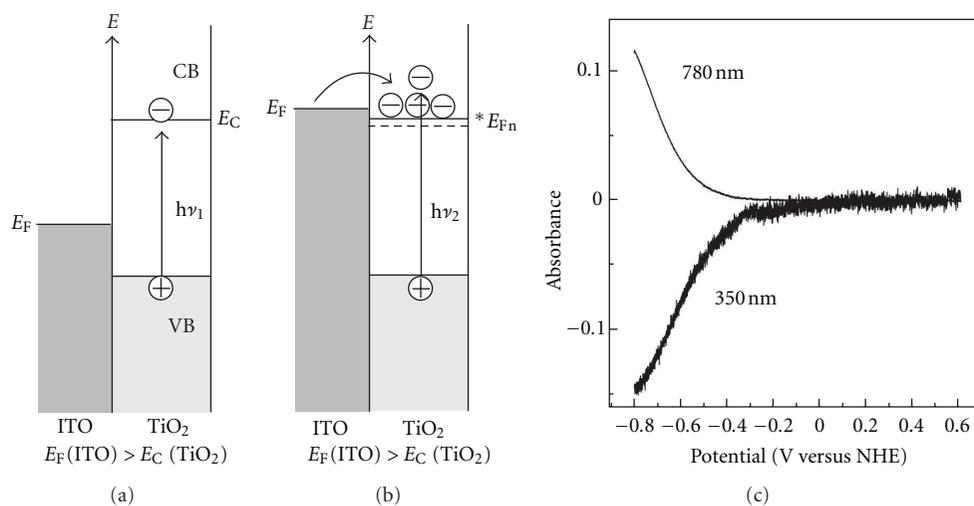


FIGURE 10: Schematic view of the principle of spectroelectrochemical determination of the quasi-Fermi level of nanocrystalline TiO₂ (a, b); for details, see the text. (c) Absorbance changes of a transparent TiO₂ film at two different wavelengths recorded during a cathodic potential sweep in a deaerated LiClO₄ (0.1 M) solution acidified to pH 2.9.

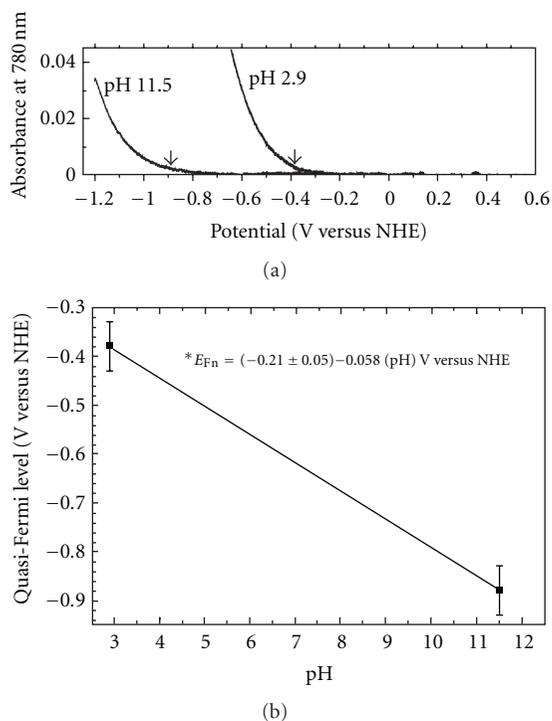


FIGURE 11: (a) Absorbance changes (at 780 nm) of a transparent nanocrystalline TiO_2 film recorded during a cathodic potential sweep in a deaerated LiClO_4 (0.1 M) solution with adjusted pH. The arrows indicate potentials at which the values of quasi-Fermi level were read off. (b) pH dependence of quasi-Fermi levels of a transparent nanocrystalline TiO_2 film. Measurements were performed outside the neutral pH range in order to avoid pH fluctuations due to reduction of protons [206].

The occupation of states near the conduction band edge results in a shift to higher energies of the bandgap absorption edge (i.e., $h\nu_2 > h\nu_1$ in Figures 10(a) and 10(b))—the so-called Burstein-Moss shift [193, 194]. From the spectroscopic point of view, this has two consequences. First, at potentials more negative than E_C (TiO_2), the difference in absorbance at wavelengths lower than the typical absorption band edge (e.g., at 350 nm) becomes negative. Second, the absorbance at 780 nm increases due to the intraband transitions of free electrons in the conduction band (Figure 10(c)) [190, 191, 195].

In this context, it should be noted that the nanocrystalline TiO_2 has often a high density of electron traps that are distributed exponentially in the bandgap below the conduction band edge [196–200]. These traps can be obviously filled at potentials slightly more positive than E_C and can also contribute to absorbance changes. This means that in practice it might be difficult to discern where exactly the rise in absorbance coincides with the potential of the conduction band edge. Figure 11(a) shows the absorbance changes at $\lambda = 780$ nm of a transparent nanocrystalline TiO_2 film at two different pH values. The potentials of ${}^*E_{\text{Fn}}$ were in this case, somewhat arbitrarily, read off at points where the absorbance change was approximately 0.005. The ${}^*E_{\text{Fn}}$ values (which

coincide with the E_C values) plotted in Figure 11(b) show a nearly Nernstian linear dependence on pH with ${}^*E_{\text{Fn}} = (-0.21 \pm 0.05) - 0.058(\text{pH})$ V versus NHE.

3.5. Quasi-Fermi Level Measurements on TiO_2 Powder Suspensions. In the field of heterogeneous photocatalysis, TiO_2 -based materials are often employed in the form of nanocrystalline powders. The quasi-Fermi level of electrons, ${}^*E_{\text{Fn}}$, can be in case of powder suspensions determined by the method of Roy et al. [29, 201] that draws on a similar method introduced previously by Bard et al. [202–204]. In Roy's method, the pH dependence of the potential of a platinum electrode immersed in an irradiated suspension of a semiconductor powder (Figure 12) is recorded in the presence of an electron acceptor with pH-independent reduction potential. As an electron acceptor, MV^{2+} (methyl viologen; 1,1'-dimethyl-4,4'-bipyridinium dichloride; $E_{\text{MV}^{2+/+}} = -0.45$ V versus NHE) [130] is typically used (Figure 12(b)).

The principle of the method is depicted in Figure 13. At the beginning of the measurement, the pH of the solution is very low and the electrons generated in the conduction band do not have enough reducing power to reduce MV^{2+} (Figure 13(a)). Upon increasing the pH of the solution, the band edges of TiO_2 shift to more negative potentials (see above Section 2.2), which makes at some point the electron transfer to MV^{2+} in the electrolyte possible (Figure 13(b)). The platinum electrode serves as a simple redox electrode in this case, and its potential shifts more negative with the increasing concentration of the reduced form of methyl viologen (MV^{+}) in the solution. The inflection point (pH_0) of the potential-pH curve (Figure 12(c)) determines the pH value at which ${}^*E_{\text{Fn}}$ coincides with $E_{\text{MV}^{2+/+}}$. Assuming Nernstian shift of band edges (0.059 V/pH unit) [125],

$${}^*E_{\text{Fn}} = E_{\text{MV}^{2+/+}} + 0.059(\text{pH}_0 - \text{pH}). \quad (14)$$

Using this procedure, ${}^*E_{\text{Fn}}$ at pH = 7 of anatase TiO_2 powder (Hombikat UV 100) was determined as -0.60 ± 0.02 V versus NHE, which is in a very good agreement with reported values for single-crystal anatase (-0.58 V versus NHE) [172]. It should be also noted that efficient scavenging of photo-generated holes is essential during these measurements. In some cases—on doped or surface-modified TiO_2 samples, for example—an additional hole scavenger must be added in order to avoid severe recombination. Such a scavenger should be very easily oxidizable (e.g., iodide), and at the same time it should not produce strongly reducing radicals upon one-hole oxidation (e.g., ethanol, isopropanol) since these are also able to reduce MV^{2+} , which would falsify the resulting values of ${}^*E_{\text{Fn}}$ [205].

4. Conclusions

TiO_2 nanomaterials play a key role in the development of various kinds of photochemical systems and devices, particularly in the field of heterogeneous photocatalysis and photoelectrochemistry. In the last years, we have witnessed a real boom of diverse strategies for fabrication of new types of TiO_2 -based materials showing an extreme variety in terms of

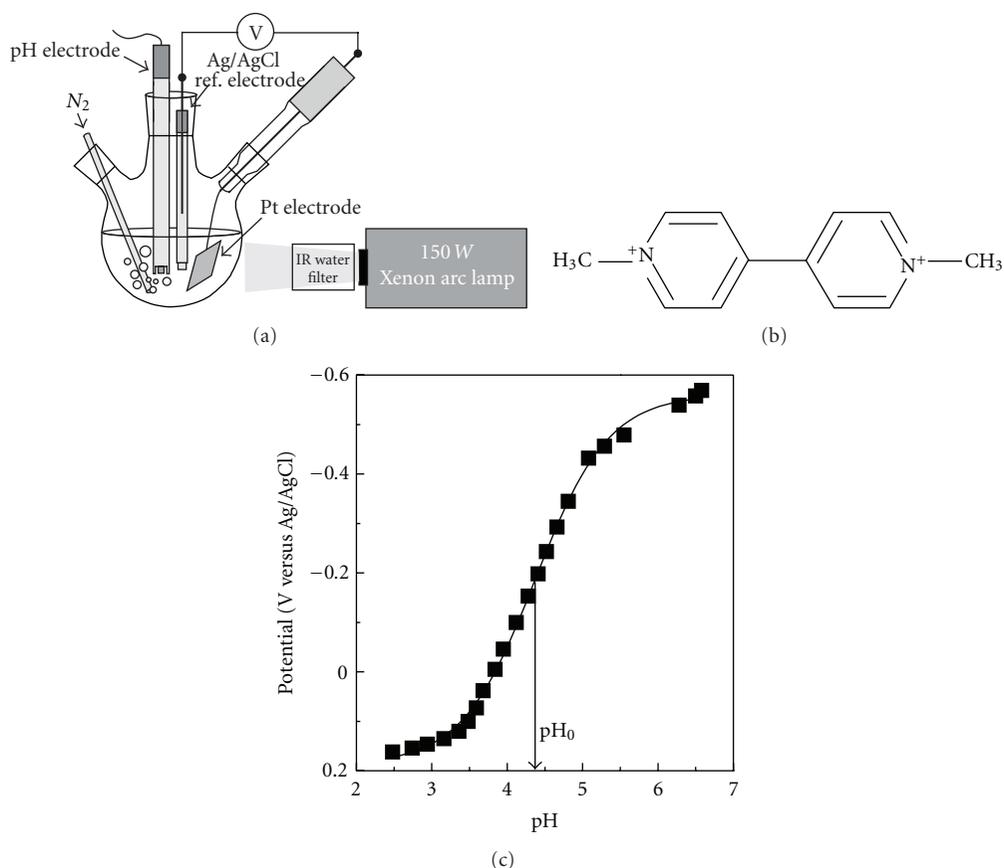


FIGURE 12: (a) Schematic view of the experimental setup for the determination of quasi-Fermi level for electrons using the method of Roy. A 60 mL solution of KNO_3 (0.1 M) with a small amount of MV^{2+} is bubbled through with nitrogen in order to avoid the reoxidation of MV^{2+} by dissolved oxygen. (b) Structure of MV^{2+} . (c) Determination of the value of pH_0 from a typical potential versus pH curve.

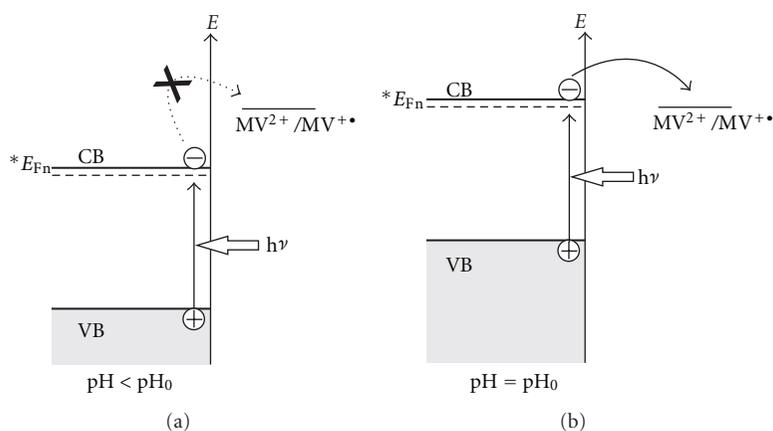


FIGURE 13: Schematic view of the principle of the determination of ${}^*E_{Fn}$. Upon increasing the pH of the solution, the band edges of a semiconductor shift to more negative potentials. At $\text{pH} = \text{pH}_0$, the value of ${}^*E_{Fn}$ matches the reduction potential of a pH-independent redox species in the electrolyte (MV^{2+}).

composition, morphology, and surface properties. Although the knowledge of the position of the band edges on the potential scale is a crucial prerequisite for understanding the photoactivity of the system and for further optimization of its performance, it has been in recent years typically only

rarely directly experimentally addressed. In this paper it has been shown that in case of TiO_2 the general strategy for band edges determination usually consists in the measurement of the flatband potential and/or the quasi-Fermi level of electrons. Apart from “classical” approaches (capacitance

measurements) developed in the field of semiconductor physics for well-defined samples in the form of single crystals, several novel techniques have been developed recently. These are particularly important since they are also suitable for measurements on non-ideal nanostructured, porous, and particulate materials, which represent the majority of currently newly developed materials. The methods discussed above included elaborate photoelectrochemical and spectroelectrochemical methods applicable on compact and nanocrystalline thin films, as well as on powder suspensions. Obviously, in case of many systems, a combination of several methods will give a more solid and complete assessment of the energetics at the solid/solution interface. It is hoped that this paper will serve as a useful resource for many scientists working in the field of photoactive nanomaterials and as an impetus for the development of further methods that will allow for better understanding and improvement of the photoactivity of photochemical systems and devices.

Acknowledgments

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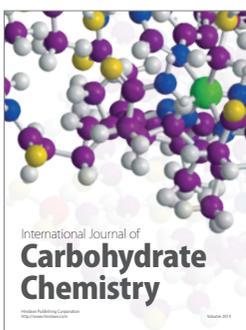
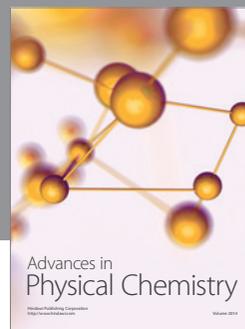
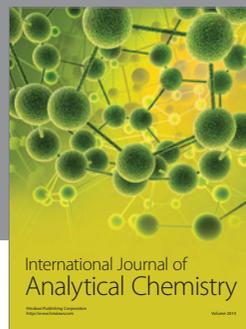
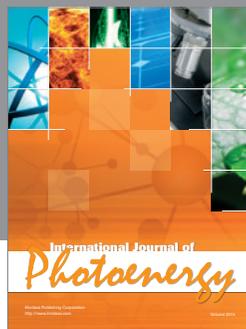
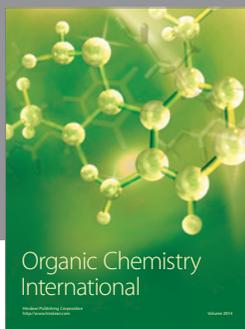
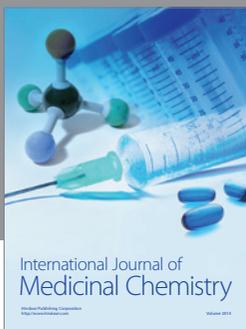
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