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The role of crystal facets and disorder on photo-electrosynthesis

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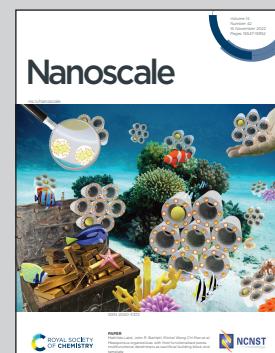
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The role of crystal facets and disorder on photo-electrosynthesis

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Photoelectrochemistry has the potential to play a crucial role in the storage of solar energy and the realisation of a circular economy. From a chemical viewpoint, achieving high conversion efficiencies requires subtle control of the catalyst surface and its interaction with the electrolyte. Traditionally, such control has been hard to achieve in the complex multinary oxides used in PEC devices and consequently the mechanisms by which surface exposed facets influence light-driven catalysts are poorly understood. Yet, this understanding is critical to further improve conversion yields and fine-tune reaction selectivities. Here, we review the impact that crystal facets and disorder have on photoelectrochemical reactivity. In particular, we discuss how the crystal orientation influences the energetics of the surface, the existence of defects and the transport of reactive charges, ultimately dictating the PEC activity. Moreover, we evaluate how facet stability dictates the tendency of the solid to undergo reconstructions during catalytic processes and highlight the experimental and computational challenges that must be overcome to characterise the role of the exposed facets and disorder in catalytic performance.

Introduction

Photoelectrocatalysis (PEC) holds the promise of providing a new paradigm for sustainable energy conversion schemes and green synthetic pathways, in favour of a circular economy, as opposed to the current fossil-based methods.[1] Solar energy is used to upgrade chemicals, rather than to deliver electricity, which explains why PEC is also termed "artificial photosynthesis".[2]

The overall mechanistic picture of the PEC process involves the use of a semiconductor material or complex semiconducting structure, where sequential steps take place, namely: (i) photon absorption, (ii) charge separation, (iii) charge transport towards the surface, and (iv) charge transfer at the interface with the liquid or gaseous medium, thus promoting the reaction.[3] Although all these steps are critical to the functional operation of materials, step (iv) brings an additional degree of complexity, when comparing to photovoltaics, since charge carriers need to drive interfacial catalytic processes with high activity, selectivity, and stability. The magnitude of this challenge explains why PV (solar to electricity) rapidly became an established technology, while PEC (solar to chemicals) is only now starting to permeate into the market with promising prototypes.[4–6]

In order to narrow the gap between the technological development of both technologies, the rational design of materials, synthetic and operation conditions of PEC systems should be built on the detailed understanding of the complex thermodynamic and kinetic properties at the semiconductor/liquid (or gas phase) interface.[7–10] In practice, this involves understanding the processes at very different length-scales, from the operation of an electrochemical cell and its losses, to how the macroscopic structure of the electrode influences the reactive area or how the atomic structure of the surface and its facets, controls the transfer of charges (Fig. 1). Achieving such control is paramount to attain a competitive performance in terms of catalytic activity, selectivity, and stability.

Crystal facets and reactivity

When crystalline solids grow, they might exhibit distinct flat surfaces that reflect the symmetry of the crystal. These surfaces are known as facets. Under thermodynamic equilibrium, facets will tend to grow aligned to the crystallographic direction with the lowest energy planes – those that maximise packing. This corresponds to the Wulff structure.[12] However, this process can be tuned to favour growth in other directions.

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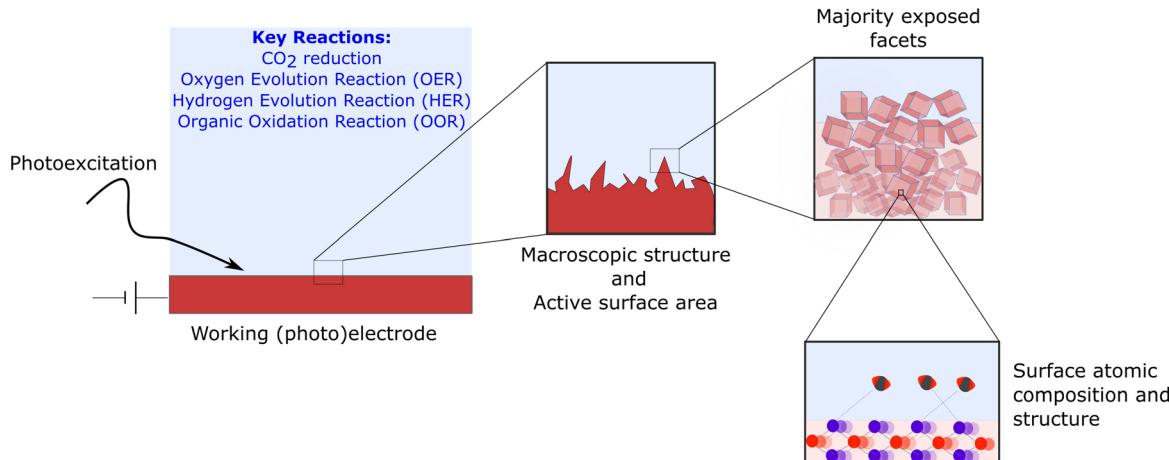
Fig. 1 Multi-scale dimension of photo-electrocatalysis and crystal facets. The development of an efficient PEC cell requires optimising a working electrode (typical area 1 cm^2 for lab-scale devices and >50 cm^2 for industrial prototypes) and the electrolyte conditions.[11] Overall optimisation takes into account the macroscopic structure of the catalyst to enhance the exposed area as well as controlling the dominant exposed facets. The energy of the surface and its atomic compositions determines the binding of intermediates and products and controls the transfer of charge across the interface.

For example, a growth-substrate can induce strain in the system and promote growth along a higher energy direction. Similarly, synthesis conditions can trigger or hinder faceting; for instance, high temperatures, close to the melting point, often favour the formation of round-shaped crystals as atoms move more vigorously. In contrast, low temperatures can stimulate the formation of sharp-edged crystals. (*See note-before reference list*) Fig. 2a shows different facets – labelled as (*hkl*) using the Miller indices in a cubic unit cell.

Tuning or exposing a specific facet has important implications for catalysis as the facets relate to the energy of the surface. Depending on the facet, the process involves breaking a different number of bonds (Fig. 2b); generally, surfaces with open surface structures and a large number of dangling bonds (*i.e.* unsaturated atoms) will exhibit a larger surface energy and thus higher reactivity.[13,14] Material scientists have the difficult task of growing and exposing large, high-energy surfaces that are very reactive towards the targeted reaction but also stable under catalytic conditions. Currently, advances in synthetic chemistry are allowing great strides in this direction. However, developments in surface characterisation are also revealing that in many cases pristine catalysts undergo reconstruction and/or disordering processes when brought to catalytic conditions in order to minimise the number of broken bonds.[15–19]
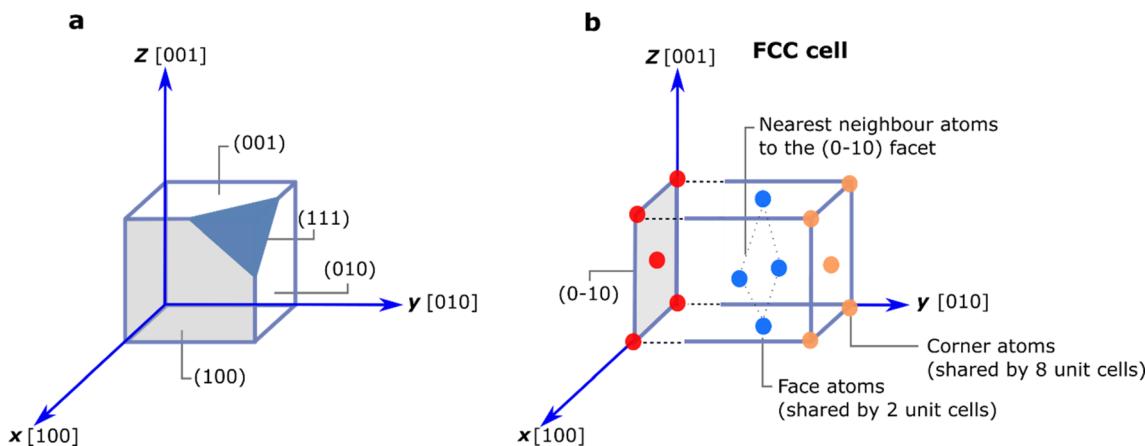
Fig. 2 Facet nomenclature and selection. (a) Different facets of a cubic crystal. *hkl* are the Miller indices that characterise the lattice plane of a Bravais lattice. (b) In a Face Centered Cubic (FCC) unit cell, the exposure of the (0−10) 2D facet (shown in red), which is parallel to the (010) facet, involves breaking 4 bonds with the nearest neighbour atoms (in blue) per atom in the facet. In general, facets that require breaking a larger number of bonds will have a higher energy. Nonetheless the system can minimise the number of broken bonds and the total energy by undergoing reconstructions and shifting atomic positions.

Facets in photoelectrocatalysis

Several recent reports have highlighted the facet dependent photoelectrocatalysis with metal oxide photoelectrodes like TiO_2, WO_3, and $BiVO_4$. For example, TiO_2 synthesised from a $Ti_7O_4(OEt)_{20}$ titanium oxo/alkoxy cluster solution using aerosol assisted chemical vapor deposition, led to a high density of exposed (010) facets, exhibiting an excellent PEC performance towards the Oxygen Evolution Reaction (OER) with an incident photon-to-current efficiency (IPCE) of ~100% at 350 nm and a Faradaic Efficiency (FE) ~90%.[20]

Similarly, in WO_3—based OER photocatalysts, synthetic strategies like laser ablation[21] or the presence of different crystal growth agents during hydrothermal synthesis,[22] led to enhanced PEC performances.[22] In particular, it was reported that the exposure of the (002) facet effectively facilitated the separation of photogenerated electron–hole pairs and suppressed the formation of peroxo species. The (010) facet was found to provide more favourable adsorption of reactive ˙OH species, leading to significantly stronger activity towards CH_4 oxidation to ethylene glycol under ambient conditions.[23]

The broad and intricate impact of crystal facets in catalytic performance is also exemplified in $BiVO_4$, a material widely used in water splitting PEC cells.[24,25] For instance, catalysts prepared by electrodeposition with the use of lactic acid were found to strengthen the atomic arrangement of the (010) orientation, which improved the transmittance of the $BiVO_4$ photoanode thin film.[26] Similarly, the development of this (010) facet in $BiVO_4$ was shown to provide adequate band bending and a deep valence band level, enhancing the production of high-value-added hydrogen peroxide (H_2O_2) with an average Faradaic efficiency of 70% from water oxidation.[27] However, there is intense debate about the reactivity of $BiVO_4$ surfaces, as discussed below.

In the following sections we outline the key roles that different facets have on photo-electrochemistry. We primarily focus on examples of $BiVO_4$ in order to provide a framework to understand the wide-ranging impact of crystal orientation on catalysis. In addition, we discuss the difficulty in stabilising reactive facets and highlight the impact that surface reconstructions and disorder have on electrode performance. Finally, we discuss the need to approach facet control from a holistic view, integrating theory and experiments, and outline exciting areas for future development.

Impact of crystal orientation on chemical reactivity

A new facet can be exposed when a crystal is split, or cleaved, along a specific crystallographic plane (Fig. 2b). Structurally, this involves the rupture of chemical bonds and the generation of a new surface composition in which atoms will have different coordination environments compared to the bulk. This plane cleavage changes the total energy of the surface, the stoichiometry of the termination and thus alters the electro-static potential leading to changes in the spatial arrangement of the atoms and the motifs exposed.[28] Moreover, the new exposed facet will also have a specific orbital orientation and will sustain a unique distribution of electronic charge both along the surface and towards the bulk.

The stoichiometry, electronic and structural patterns that emerge when selecting a specific facet have a direct impact on the catalytic properties of semiconductors.[29,30] First, a new exposed facet can change the energy of the frontier orbitals (Conduction Band Minima and Valence Band Maxima, CBM and VBM, respectively) and the Fermi level, impacting band alignment and band bending (Fig. 3a).[31–33] Second, the new surface termination changes the adsorption energy of reactants, intermediates and products, thus modifying reaction mechanisms and product distributions (Fig. 3b). Third, the new surface energetics might favour the formation of defects and polarons (Fig. 3c) with implications for both reaction mechanisms and the transport and accumulation of charges (Fig. 3d).[34–36] Finally, a new surface termination might influence the ability to deposit co-catalysts for enhanced performance (Fig. 3e) and change interface energetics and the molecular structure of the electrochemical double layer (EDL) (Fig. 3f).[37–39]

In the next sections, we discuss the different role of facets and disorder; for clarity we focus on examples of $BiVO_4$. This metal oxide has a monoclinic crystal structure and belongs to the C^6_{2h} point group and the space group $C2/c$ (no. 15 in the international tables for crystallography) in the conventional setting, which is used here. Note that different settings, such as the body centered $I2/b$ setting, where the axis and facet notations vary, are sometimes used in the literature.[40] Its most stable cleavage plane is orthogonal to the [010] direction, along the longest crystallographic axis in the $C2/c$ setting. The resulting (010) facet is composed of 6-fold coordinated Bi atoms, 4-fold fully coordinated V atoms and 2-fold coordinated O atoms (Fig. 4a).[41] This facet has been found to possess good reactivity towards water oxidation and is usually present in high-performing $BiVO_4$-based PEC cells.[42,43] The second most stable surfaces include the chemically similar (110), (−110), (−111), and (11−1) facets. Together, they actually provide the largest surface in a thermodynamic equilibrium, as expressed by the Wulff construction.[44] Other facets can also be prepared,[40] such as the (001) that contain 4-fold and 5-fold coordinated Bi atoms instead.[31]

Band alignment and intermediate adsorption

Theoretical studies have shown that the exposed facet in $BiVO_4$ influences the band energies. While all facets exhibit a highly oxidising VBM (high position in the energy scale), suitable for OER, the CBM of (010) is more positive than the H^+/H_2 equilibrium potential, and thus the termination is unreactive towards the hydrogen evolution reaction (HER). Structure sensitivity is clear for this material as, for example, the CBM of the (001) facet is suitable for proton reduction making this facet a good candidate for the full water splitting reaction.[31,33] Similar behaviour is observed in p-type Cu_2O in which the
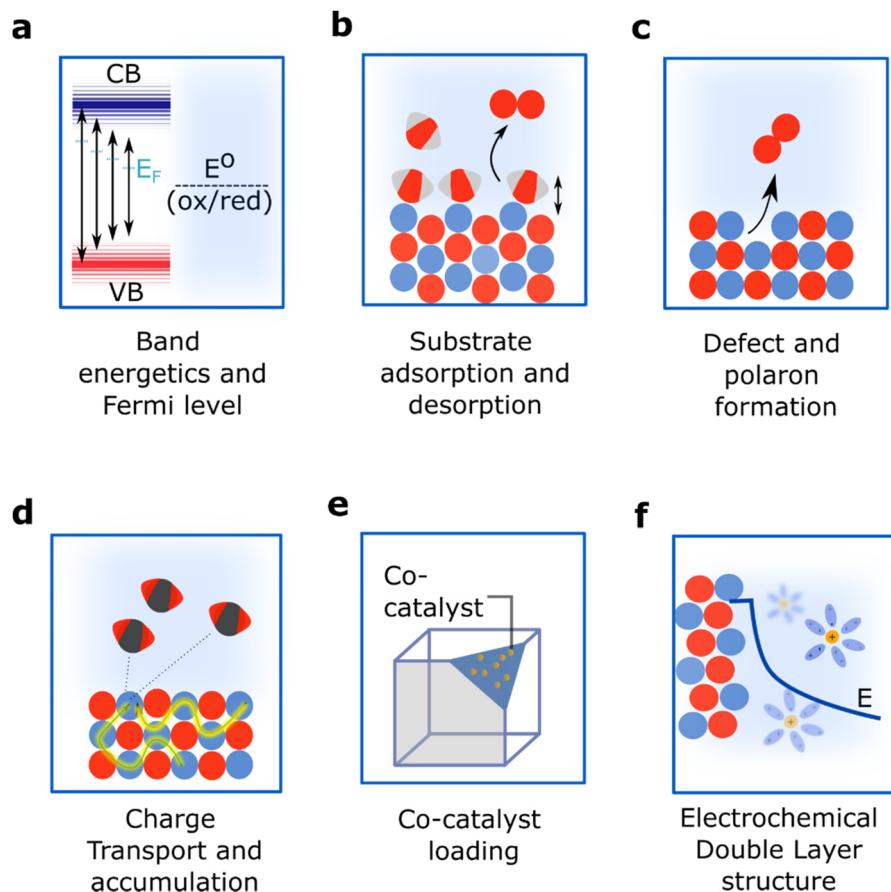
Fig. 3 The role of facets on semiconductor photoelectrocatalysis. The exposed facet will influence (a) the energy of the valence and conduction bands as well as the Fermi level (E_F) thus influencing the equilibration with the electrolyte redox level ($E°$) and the band bending (b) the energy of adsorbates, (c) the tendency to form defects (and polarons) at the surface, (d) the ability of charge carriers to move through the surface and towards the bulk of the solid, (e) the selectivity to deposit co-catalysts and (f) the molecular structure of the interface.

CBM of rhombic dodecahedral (110)-dominated oxide is more positive than that of the cubic (100) faceted Cu_2O. Moreover, the Fermi level of the rhombic Cu_2O is located at a more positive potential leading to larger band bending upon equilibration.[36]

In addition to these effects, modelling of the OER mechanism in $BiVO_4$ has also revealed that the (110) and (−110) surfaces exhibit more favourable energetics for the reaction compared to other facets. The authors, attributed this to a stronger adsorption energy for the O* intermediate that is generated from the oxidation of adsorbed H_2O.[33]

Defect formation and surface reactivity

Preparation of oxides is mostly performed through thermal treatments; thus, these semiconductors are prone to lose oxygen, generating vacancies and leaving uncoordinated atoms in the lattice.[45–49] The resulting defective surface or material can be thermodynamically stabilised by structural rearrangements, in which atoms attempt to maximise their coordination number. This ability of a surface to stabilise a vacancy is closely related to the properties of the constituent atoms and

consequently, defect formation is facet dependent. Indeed, in $BiVO_4$ the (010) facet has been found to sustain oxygen vacancies that are stabilised by a splitting mechanism (Fig. 4a).[34] The presence of these vacancies has been found to influence OER catalysis. It has been proposed that these defects change the OER reaction mechanism by providing new active sites as well as by lowering energy barrier for the first Proton Coupled Electron Transfer (PCET). This occurs because the vacancy-associated electrons are more readily available for transfer (Fig. 4b).[35,50] Vacancies might also provide additional pathways *via* hydration, which further influence the reaction mechanism (Fig. 4c).[35] In addition, oxygen depletion has been experimentally observed to increase the selectivity towards the oxygen evolution reaction, in detriment of the competing H_2O_2 formation.[51] On the other hand, hydrogen peroxide production is predicted to be more favourable in vacancy-free (−111) surfaces.

It is important to note that the role of defects in catalysis is controversial and there are discrepancies between theoretical and experimental work. For example, in Fe_2O_3 photoanodes, DFT + U calculations have suggested that the potential deter-
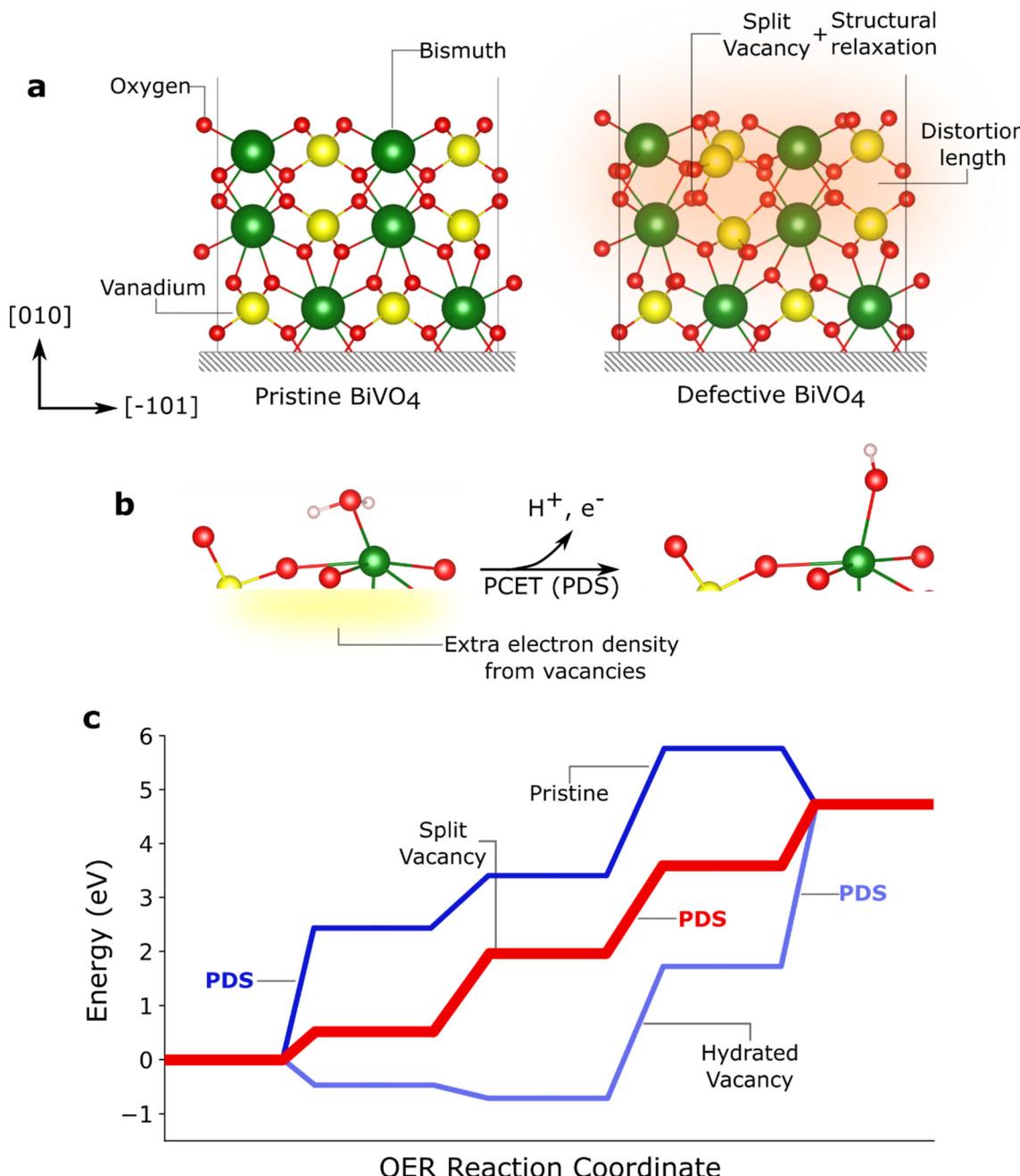
Fig. 4 Role of crystal facets on the formation of defects. (a) Pristine and defective $BiVO_4$ showing how the formation of a split vacancy defect changes the atomic positions along the [010] direction (labelled [001] in the *I2/b* setting in ref. 34 and 35). The shaded orange area indicates the extent of the structural distortion and movement of atoms due to the formation of the defect. (b) Diagram showing how the presence of a split oxygen vacancy introduces extra electrons which can be more readily removed from the system, lowering the Potential Determining Step (PDS) and enabling a more favourable mechanism. (c) Gibbs free energy profile of the Oxygen Evolution Reaction (OER) on the (011) $BiVO_4$ surface. The step with the highest energy is the PDS. Figure a was adapted from ref. 34 and figure b and c were adapted from ref. 35.

mining step (PDS) during OER is reduced when increasing the density of oxygen vacancies compared to a pristine surface.[52] However, kinetic analysis in Fe_2O_3 containing different vacancy concentrations have shown that the OER rate deter-mining step (RDS) is chemical in nature and is independent of the vacancy concentration.[53] Such discrepancy might be related to the chemical nature of the RDS[54,55] or to the difficulty in experimentally separating the contributions of vacancies within a large surface. As discussed below, further studies integrating modelling and experiments, are needed to unambiguously expose the role of defects and disorder in the catalytic mechanisms.

Charge transport and accumulation

A further consequence of defect formation is the introduction of electronic charge into the lattice. For example, the formation of an oxygen vacancy results in the injection of two electrons into the structure. Such excess charge might minimise its energy by displacing the surrounding atoms forming a polaronic state and change the conductivity of the material. Polarons can also be formed upon photoexcitation.[7,56–58] The tendency to form polarons depends on the atomic structure surrounding the charge and is, consequently, facet-dependent. Indeed, recent experiments have shown that the timescale of polaron generation at the bulk is different than at the surface, suggesting that the coordination environment is a critical parameter.[59,60]

Achieving high catalytic activities requires an efficient transport of photogenerated carriers to active sites and the accumulation of charges for a sufficient amount of time (*i.e.* beyond milliseconds to drive the OER).[61] Photocatalytic oxides typically exhibit anisotropic charge transport – different crystal directions show different transport properties. Moreover, charge carriers often move *via* thermally activated hopping mechanisms, requiring geometric changes in the atomic structure for effective polaron motion. As expected for a polaronic system, in $BiVO_4$ the activation barrier for electron (approx. 0.2–0.6 eV) and hole (approx. 0.4–0.8 eV) hopping are highly anisotropic leading to directional dependent mobility.[37] A direct consequence of such anisotropic transport is a facet dependent charge accumulation: the (010) facet has been experimentally observed to favour electron accumulation while holes are more readily available at (110) terminations.[39,42]

Maximising charge transport and controlling the localisation and accumulation of long-lived charges is critical for photoelectrochemical reactions. For example, the rate determining step of the OER in Fe_2O_3 photoanodes has been measured to involve the diffusion of three oxidation equivalents to the active site, thus requiring an efficient transport mechanism.[62,63] Similar observations have been made in other catalytic oxides, including $BiVO_4$, yet the role of the exposed facet on the kinetics of the rate determining step is largely unknown.

Co-catalyst deposition and electrochemical double layer structure

Anisotropic accumulation of electrons and holes implies that some facets might be more likely to act as reduction or oxidation sites respectively. This has a direct consequence in co-catalyst deposition which normally involves the photo-reduction of ions into a metallic catalyst (*e.g.* Pt, Au) or the photo-oxidation of ions into oxides (*e.g.*: MnO_2). Experimental studies with $BiVO_4$ have found that metals selectively deposit on the (010) facet, while oxides are selectively formed at the (110) facet.[39]

The role of the selected facet in controlling the distribution of surface charge in solid electrodes has also an impact on how the electrochemical double layer (EDL) is established when the electrode interfaces a liquid electrolyte. In particular, different facets might exhibit a different potential of zero free charge (*pzfc*)—the potential at which the capacitive charge at the surface is zero.[64] This is important because the *pzfc* dictates the strength of the interfacial electric filed, which depends on the difference between the *pzfc* and the applied potential.[38] Consequently, the facet-dependent *pzfc* will influence the molecular structure of the electrode-electrolyte interface and impact the rate of charge transfer.

Furthermore, the different atomic arrangement on each facet influences the molecular arrangement of the electrolyte molecules. For instance, hematite immersed in water forms hydrogen bonds with its (012) and (110) facets, while its (001) facet reorders the water structure only weakly.[65] Despite the recognised importance of understanding the role of the structure of the EDL on the electrochemical activity, theoretical and experimental assessments are scarce. Theoretical modelling of the atomic structure of the EDL requires molecular dynamics (MD) simulations with explicit inclusion of solvent molecules. Those can be done *via* parametrised force-fields,[65] which typically lack transferability, or *ab initio* approaches.[66,67] The latter are computationally expensive if one aims to reproduce long-range effects in the solvent but significant progress has been made over the last years.[68,69]

It is important to note that, to date, experimental studies are often limited to metallic surfaces. While in semiconductor catalysts the potential drop occurs primarily within the solid, forming a space charge layer,[70,71] the ability to charge the surface is likely to impact the molecular structure of the electrolyte and consequently impact reactivity. To date, this is an uncharted territory.

Determining the best facet for photocatalysis is particularly difficult as many processes, ranging from light absorption to the desorption of reaction products, should synchronise. Therefore, the optimal facet might not be the one that is most reactive, or more prone to form active defects, but the one that best balances the different steps involved in the photocatalytic mechanisms. Addressing such complexity necessarily requires a holistic approach to facet engineering involving *in situ* characterisation and theory guidance.

Facet stability and control

Thermodynamic stability and surface reconstructions

The dynamic rearrangement of materials under photoelectrochemical conditions is a largely unexplored area. To a first approximation, the driving force behind these rearrangements is the maximisation of the crystal packing and the atomic coordination once the solid is in contact with the electrolyte. However, photo-electrosynthesis is a dynamic process and the electrochemical conditions (pH, ionic strength...) might vary during the reaction inducing structural transformations in the electrode. For example, during a reaction, a pH gradient might develop rendering a specific crystal phase unstable and trigger a solid—solid phase transition.

Recent work has stated to explore the correlation between the reconstruction of a specific facet and catalytic selectivity. These studies have primarily been performed in well-defined metallic surfaces. For example, *operando* AFM has been used to observe changes in the surface morphology of a Cu(100) cathode for CO_2 reduction as a function of potential.[18] The authors proposed a correlation between the reconstructed surface at different potentials with CO_2 reduction intermediates, such as CO species, in order to explain the bias dependence of the product selectivity.

Reconstructions have also been proposed to be an integral part of the catalytic cycle.[7,72–74] For example, in oxides like IrO_2 and Co_2O_3 used for the OER, isotopic labelling studies have shown that some of the O_2 formed contains lattice oxygen atoms.[75,76] Similar observations have been made for TiO_2 both for the OER and the oxidation of organic compounds such as benzene.[77–79] In contrast, $NiFeO_xH_y$ surfaces have been shown not to lose lattice oxygen during the OER but Fe is incorporated from the electrolyte.[80–82] The reactivity and the tendency to undergo reconstructions will depend on the crystal facet and the specific terminations, for example, hydroxylated disordered structures are known to work better than the organised rutile terminations.

The preferential dissolution of the different elements in the salts under the electrolyte potential and photocatalytic conditions is a major issue which is poorly explored due to its complexity. Yet, indications of leaching of cations (under positive potentials) and anions (at negative ones) start to be gathered.[83,84] The ultimate consequence of such leaching is that surface disorder appears, leading to atom-enriched surfaces, new structural motifs, and disorder in the packaging of polyhedral subunits or the materials themselves. Disorder allows for a fine adjustment of the electronic levels that can be accommodated by the extra degrees of freedom on the surface of the material.

Synthetic manipulation of facets

The ultimate goal of manipulating the crystal structure through the control of the exposed facet is to achieve a highly reactive surface. However, as with the reconstructions, very reactive facets usually rapidly disappear during the crystal growth process while facets with lower surface energy grow slower, giving rise to the final shape of the crystal. As a consequence, special synthetic methods are required to stabilise reactive terminations such as selective etching, kinetic and thermodynamic control. One powerful method explored to prepare catalysts is to use organic and inorganic additives as Morphology Controlling Agents (MCAs), which act as selective surface stabilisers during synthesis. MCAs adsorb on specific terminations reducing the surface energy and deviating the crystal growth from its thermodynamically preferred path.[14,85,86] Typical MCAs are: Poly Vinyl Pyrrolidone (PVP), Cetyl Trimethyl Ammonium Bromide (CTAB), Sodium Dodecyl Benzene Sulfonate (SDBS), stearic acid, oleic acid and potassium iodide (KI). Importantly, these stabilisers must be removed to obtain a clean surface before the solid can be used

in photoelectrocatalytic applications. While facet control in metal oxides is a challenging topic, there have been important synthetic advances and we refer the readers to reviews on this topic.[87,88]

Challenges and outlook

Since the pioneering work by Fujishima and Honda in the early 70s, photo(electro)chemistry has made great strides thanks to synthetic advances powered by better mechanistic understanding. Such has been the success that, in many cases, the technology is becoming commercially viable. Given the demand for ever more complex chemicals, the next step in the design of photoelectrocatalytic materials is, unavoidably, going to involve the fine tuning of the reactive surface in order to drive selective multi-electron chemistry (*e.g.* CO_2 reduction into targeted C_{2+} products).

Such control will require better understanding of how the electrochemical surface evolves during catalysis and identifying how to prepare not the *pristine* solid, but the active catalyst. In this context, recent technological advances are opening the door to *operando* and *in situ* studies.[89–91] This includes exciting opportunities in microscopies, such as transmission electron and atomic force microscopies (TEM and AFM, respectively), as well as spectroscopies, such as IR, Raman and X-ray absorption, photoelectron and emission spectroscopies (XAS, XPS and XES, respectively).[92–96]

Experimentally, one challenge that lies ahead of performing these advanced *operando* studies, will be to establish whether the observed surface changes result from the catalytic reaction or the measurement itself. For example, it has recently been shown that a chemical segregation of Bi in $BiVO_4$ crystals takes place during TEM measurements forming Bi nanoparticles on the photoanode surface.[97] Indications seem to point out towards a preferential dissolution of vanadyl species (Bi presenting a lower detachment rate). Accounting for these processes and transformations is crucial to understand the real surface structure that determines the structure-activity relationships governing the photoelectrocatalytic process. Such mechanistic understanding is only nowadays beginning to be experimentally probed and introduced in the simulations.[98,99]

Beyond the monitoring of the surface, efficient catalyst development requires identifying how the surface changes correlate with reactivity and selectivity. This will entail the further coupling of optical spectroscopy and microscopy with product detection methods such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Differential Electrochemical Mass Spectrometry (DEMS) or on-line Electrochemical Mass Spectrometry (EC-MS) as well as the close integration of characterisation techniques with first principles modelling.

From a theoretical viewpoint, to understand how disorder and facet changes influence reaction mechanisms, product distributions and reaction selectivity, it is going to be crucial to establish how the reconstructions of the solid during cataly-

sis change the electronic structures and surface motifs. This will require modelling at different time and length scales as well as establishing the origin and control of the preferential dissolution. Importantly, it will also demand explicitly introducing disorder in the simulations;[100] this is essential to provide meaningful structure-activity relationships, since lowering the symmetry of the materials can break linear-scaling relationships that limit the activity or selectivity in catalysed processes.[101] Despite the complexity of the photoelectrocatalytic process, the recent advances in synthesis, characterisation, and simulations will ensure an exciting and thriving future for photo-electrosynthesis research and development.

Note

Information about facets and more generally about crystallography can be found in these useful sites: (i) https://www.its.caltech.edu/~atomic/snowcrystals/faceting/faceting.htm (ii) https://sethna.lassp.cornell.edu/CrystalShapes/Equilibrium_Crystal_Shapes.html (iii) https://www.xtal.iqfr.csic.es/Cristalografia/index-en.html.

Conflicts of interest

There are no conflicts to declare.

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