

Reading at exposed surfaces: theoretical insights into photocatalytic activity of ZnWO₄

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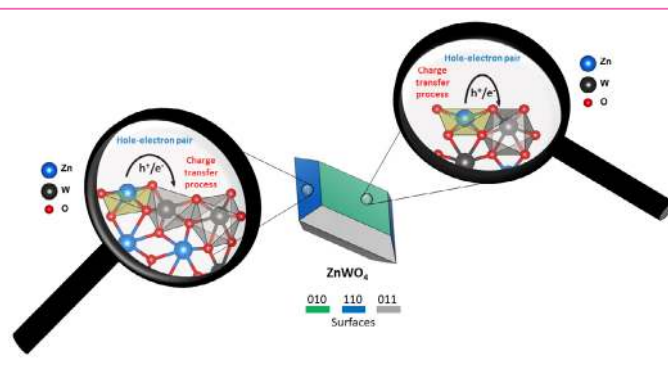
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ABSTRACT: Understanding the criteria warranting the existence, stability, and activity of a given configuration of atoms has pivotal relevance in chemical and materials science. Photocatalysts, traditionally semiconductors, are essential for processes ranging from water purification to water splitting, air filtration, and surgical instrument sterilization, and harvest optical energy to drive chemical reactions. These semiconductors harvest optical energy to drive chemical reactions. With chemical reactions dictated by atomic and molecular interactions at the



nanoscale, examining these processes with near-atomic resolution is necessary to understand photochemical processes in depth and to improve materials for next-generation catalysts. The performance and key electronic properties of semiconductors are dictated by the interplay between the surface chemistry and morphology, whose manipulation has inspired experimental and theoretical researchers. This interplay has been clarified by theoretical studies based on atomic-scale modelling with particular attention given to two sets of degrees-of-freedom: the atomic positions and chemical configuration. This perspective article presents the major computational challenges and modern methodological strategies toward advancing the field. The ZnWO₄ material was selected as a case study, and the key concepts developed in recent years are discussed to clarify the morphology, i.e., the exposed surfaces of materials, and explain its functional properties or performance. First-principle calculations capture the geometric and electronic effects on the photocatalytic activity in agreement with experimental data. Indeed, important and often surprising structure-function relations have been observed based in depth atomistic modelling on morphological analysis. An overview of past achievements and future directions is provided according to the authors' outlook.

Keywords: ZnWO₄; First-principle calculation; Geometric effect; Electronic effect; Photocatalytic activity; Atomistic modelling

MORPHOLOGY THAT MATTERS

Although controlling the geometric shape taken by an inorganic material may be initially considered as scientific curiosity, its implications go far beyond aesthetic appeal. Morphologies are important in chemistry and materials science. The morphology control of materials from the nanoscopic to the macroscopic scales can contribute to the improvement and induce the emergence of properties^{1,2}. A recurring theme with regard to the surface chemistry of many materials is the control over the morphology of crystals, which is a very active area of research because most of the physical and chemical properties are shape-dependent. The morphology does not only control the material's physicochemical properties, but also determines its relevance and merit with regard to technological applications³⁻⁶.

Anisotropy is a basic property of single crystals, by which they exhibit different physical and chemical properties on various surfaces and in diverse directions. The surface properties of materials are highly depended on the material's morphology, which is composed of different exposed crystal surfaces. These exposed surfaces display a different surface atomic arrangement and local coordination. At the atomic level, the surface atoms have lower coordination number than those in the bulk; consequently, those surface atoms with changed atomic structure and free energy exhibit high chemical reactivity. Such characteristics entail surface chemistry treatment a favored approach for various applications⁷⁻⁹. The micro- and nano-crystal morphology significantly influences the end-use efficacy of these solid products, which improves the properties of functional materials, such as the reactivity of catalysts, i.e., the performance of catalytic processes depends on how the desired

reactions are favored at the exposed catalyst surfaces. This is decided by the number and nature of the active sites and the catalytic efficiency¹⁰⁻¹⁵, the bactericide and sensor activities, and so on. To maximize the exposed surface for a given load catalyst at the nanoscale, metal nanoparticles have been widely employed in a wide range of catalytic systems¹⁶⁻¹⁸. In particular, the growth process of polyhedral crystals has been explored with significant interest not only due to the emergence of new or enhanced properties from selected crystal surfaces, but also due to the opportunity for fundamental studies on the control nucleation and growth kinetics involved along the crystallization mechanism¹⁹.

In recent years, several studies have attempted to establish correlation between the morphology, properties, and applications for both micro- and nano-materials²⁰⁻²⁷. For example, in the field of catalysis, the presence of high-index facets at the crystal morphology is more desirable, in comparison with their low-index faced counterparts, because they have low coordinated surface atoms that are exposed on such facets, which can serve as highly catalytic active sites²⁸⁻³⁰. A high-index facet has a higher density of under-coordinated atoms, steps, edges, and kinks that serve as preferred, highly active catalytic sites³¹⁻³⁴. Depending on the arrangement and distribution of surface facets, nanocrystals with a high-index surface can be prepared with different morphologies. In the case of noble-metal nanocrystals, it is well known that the exposed surfaces are terminated in low-index facets such as (110), (111), and (100) surfaces, owing to their low specific surface free energies relative to other surface types³⁵. For example, the most reported morphologies of Pt nanocrystals are octahedrons composed of (111) surfaces³⁶⁻³⁸, cubes dominated by (100) surfaces³⁸⁻⁴³, and cuboctahedrons wherein both the (111) and (100) exposed surfaces appear^{44,45}. However, when high-index surfaces in the morphology of noble-metal nanocrystals are obtained, a substantial enhancement of catalytic activities is observed^{33,46}.

Druce et al.⁴⁷ have presented an experimental study, wherein they demonstrated that perovskite oxide ABO_3 surfaces always exhibit AO-surface termination when exposed to elevated temperatures under high oxygen pressure. Consequently, the catalytically active transition metals on the B-site are buried in the subsurface layer, while the A-site cations are exposed at the solid/gas interface. Additionally, Staykov et al.⁴⁸ concluded that the catalytic activity of the AO-terminated perovskite surfaces strongly depends on the presence of surface oxygen vacancies, which expose the electronic states of the BO_2 -sublattice to the gas/solid interface. In particular, the electronic properties in the vicinity of the surface oxygen vacancies of $SrTiO_3$ have shown that such vacancies are not simply spatial voids, but rather regions in space that are characterized by high electron density⁴⁹. Because of the molecular oxygen activation and dissociation in an electrophilic reaction, surface oxygen vacancies are the preferred surface active sites. Additionally, the oxygen vacancies on the SrO surface of $SrTiO_3$ exhibit the tendency of pairing, owing to the electronic relaxation in the vicinity of the vacancy pair⁴⁸. In this context, Feng et al.⁵⁰ have summarized the recent progress of research on the crystal facet tailoring arts in perovskite structure oxides.

SEMICONDUCTOR MATERIALS

Photocatalysis is an appealing approach toward tackling environmental and global energy problems. Over the past decade, semiconductor photocatalysts with tailored morphologies have attracted intense research interest in many research fields, such as the photocatalytic degradation of pollutants⁵¹, water splitting⁵²⁻⁵⁴, and photocatalytic antibacterial fields^{55,56}, owing to their many intrinsic shape-dependent properties^{57,58}. Additionally, the exposed surfaces appearing on the morphology do not only determine the intrinsic physical and chemical properties, but also provide new technological applications in catalysis, optics, electronics, and magnetics. Extensive investigations have been carried out with regard to the dependency of the surface on photocatalytic activity⁵⁹⁻⁶¹. Generally, exposed surfaces play a key role in the photocatalytic efficiency by involving three main factors: (i) by tuning band electronic structures^{62,63}; (ii) by providing high active facets/sites⁶⁴; (iii) by increasing the selective oxidation or reduction activity⁶⁵.

In this context, McLaren et al.⁶⁶ reported that the photocatalytic activity of ZnO depends on the fraction of the exposed (001) surface's crystal face. Xi and Ye⁶⁷ reported that $BiVO_4$ with (100) exposed surface facets displays an enhanced photocatalytic activity for Rhodamine B (RhB) degradation and O_2 evolution. Moreover, Li et al.²² have demonstrated that the (110) surface of $BiVO_4$ enhanced the photocatalytic activity. In Ag_3PO_4 , rhombic dodecahedra morphology with (110) exposed surfaces exhibits much higher activities than cubes with (100) exposed surfaces for the photocatalytic degradation of organic contaminants²⁰. Zhang et al.⁶⁸ have investigated the photocatalytic oxidation activity order of $NaNbO_3$ with low-indexed surfaces. Many exposed surfaces in different semiconductor photocatalysts have been shown to be efficient in increasing photocatalytic activities, such as (001) in TiO_2 ⁶⁹ and (100) in WO_3 ⁷⁰. Very recently, Lu et al.⁷¹ reported that the $BaZrO_3$ nanocrystals with the (001)/(011) facets and a corresponding higher reduction capacity could effectively improve the photocatalytic hydrogen evolution in pure water.

An advanced understanding of the chemical and physical factors determining the properties and performance of semiconductors is an obvious prerequisite toward the systematic improvement of their mobility and stability. In our laboratories, it has been a long-standing objective to develop platforms that enable the experimental and computational investigation of semiconductors through modeling. In this research field, our group has developed different semiconductors such as $\alpha-Ag_2WO_4$, $Ag_3PO_4:Mo$, $PbMoO_4$, $HA@Ag$ (hydroxyapatite decorated with silver), $ZnWO_4$, $NiWO_4$, and $\alpha-AgVO_3$ with good performance as photocatalytic materials for the degradation of organic dyes⁷²⁻⁷⁶ and antibacterial agents⁷⁷⁻⁸¹.

In simple terms, a photocatalytic reaction on a semiconductor includes at least five main steps⁸²: i) light absorption by the semiconductor, ii) formation of photogenerated electron (e^-) and hole (h^+) pairs. The optical absorption induces the transfer of electrons from the valence band (VB) to conduction band (CB), generating the electron/hole (e^-/h^+) pairs⁸³. iii) migration and recombination of the photogenerated electron-hole pairs. After these transfer processes, e^- and h^+ are capable to migrate from the bulk to the surface to participate in oxidation and reduction reactions, respectively. Meanwhile, electrons and holes can also

recombine and dissipate heat in the pathway of transport to surface, which produces negative effect on photocatalysis. iv) adsorption of reactants and desorption of products, and v) occurrence of redox reactions on the semiconductor surface. A schematic representation of the different steps along the photocatalytic process on a typical semiconductor is presented in **Figure 1**.

The behavior of the e^- and h^+ charge carriers at the semiconductor surfaces controls the performance of important applications, including photocatalysts and solar cells⁸⁴, because the photocatalytic reaction occurs only when photo-excited e^- and h^+ are available on the surface^{85,86} and need to be efficiently separated and transferred away from each other to enhance the performance. The nature and mechanisms by which e^- and h^+ form, and their role in photocatalysis, remain uncertain. Moreover, e^- can transport through the material potentially trapped at the lattice sites in the bulk or at the surface. Thus, they can affect the conductivity and interaction with the surface-adsorbed species. Then, e^- can potentially promote conductivity in the material or affect the surface reaction mechanisms. However, they can also form carrier recombination centers, which are detrimental to photoconductivity. These charge carriers in oxide semiconductors can be delocalized or can be self-trapped to form small polarons⁸⁷.

When a photocatalyst absorbs light, it generates electron/hole (e^-/h^+) pairs such that electrons and holes can react with water (H_2O) and dissolved oxygen (O_2) separately to generate reactive oxygen species (ROS)^{88,89}. These ROS, such as the hydroxyl radical ($OH\cdot$), superoxide radical ($O_2^{\cdot-}$), and singlet oxygen (1O_2), are capable of disinfecting pathogens by damaging the essential macromolecules and active agents to react with the exposed surfaces of the semiconductor. Additionally, they are responsible for the corresponding photocatalytic activity. Photocatalytic activities are also closely related to their electronic structures, and the value of the band gap determines the light absorption range of the semiconductor and the number of photo-generated e^-/h^+ pairs. Additionally, the positions of the CB bottom and VB top are key considerations in explaining

the reduction and oxidation abilities of photogenerated electrons and holes, respectively. From a thermodynamic viewpoint, the reduction potential of the electron acceptors should be energetically below the CB bottom of a semiconductor, while the oxidization potential level of the electron donors should be above the VB top. A deep position of the VB implies a high cost of extracting electrons from the $2p$ levels of the O_2^- anions. A high CB position implies a moderate tendency toward accepting electronic charge, which results in low reactivity and chemical inertness. Moreover, the value of the band gap size is also important because it determines the light absorption range of the semiconductor and the number of photo-generated electron/hole pairs. For example, Yu et al.⁹⁰ prepared $FeWO_4$ samples with different morphologies by varying the pH values during the hydrothermal process, and systematically investigated their optical properties. Their results revealed that the band-gap values of $FeWO_4$ correlated with specific morphologies. From a thermodynamic viewpoint, the reduction potential of the electron acceptors should be energetically below the CB bottom of a semiconductor, while the oxidization potential level of the electron donors should be above the VB top.

Amongst all factors influencing the photocatalytic activity, the morphology and exposed surfaces play a major role by providing a higher surface area, which leads to the higher adsorption of dye molecules on the surface of the photocatalyst, and to the enhancement of the photocatalytic activity. Then, the surface controlled synthesis of materials, i.e., crystal facet engineering, is not only a promising method of promoting the e^-/h^+ separation and then inducing the formation of active ROS ($OH\cdot$ and $O_2^{\cdot-}$ radicals and singlet oxygen 1O_2) to improve the photocatalytic activity of semiconductor-based photocatalysts⁹¹⁻¹⁰¹, but also a rational procedure for investigating the relationships between the surface structures and the photocatalytic properties to develop highly active photocatalysts. Then, crystal-facet engineering plays a central role in the kinetic and thermodynamic modulation of redox reactions at the catalyst's surface¹⁰²⁻¹⁰⁶. Generally, the highly active facets correspond to high-index facets end owed with a more reactive atomic arrangement, termination, and local coordination¹⁰⁷⁻¹¹⁰. For example, the results obtained by theoretical and experimental studies reveal that the (001) surface of anatase TiO_2 is much more reactive than amore thermodynamically stable (101) surface, and that the (001) surface may in fact be the dominant source of active sites for various applications¹¹¹⁻¹¹⁴. The surface energies of the (010), (001), and (101) surfaces have been theoretically calculated and reported as $0.53 Jm^{-2}$, $0.90 Jm^{-2}$, and $0.44 Jm^{-2}$, respectively. As can be seen, the surface energy of (010) is slightly higher than that of (101) and much lower than that of (001)¹¹⁵. Therefore, it has been reported that faceted- TiO_2 with a high percentage of (010) facets exhibits a similar photocatalytic activity with the (001) facet^{116,117}. Very recently, Carey and McKenna¹¹⁸ provided crucial insights into the behavior of e^- and h^+ in TiO_2 . These applications are relevant for applications in photocatalysis, and have challenged the common perception where by electrons are trapped at the low index surfaces of anatase TiO_2 .

Heterogeneous catalysis is another interesting example, where in the many reactions occurring on the surface

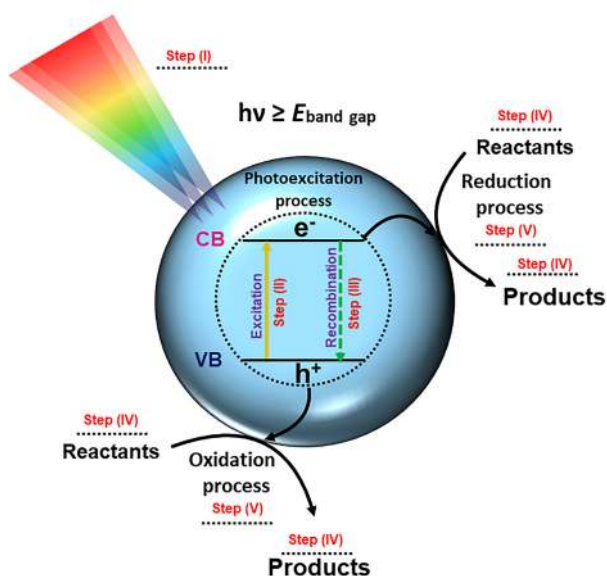


Figure 1. Schematic representation of photocatalytic process.

catalysts are highly sensitive, in terms of activity and/or selectivity, to the arrangement (or the coordination number, more precisely) of atoms. Thus, the surface type on the surface is determined by the geometric shape of the micro- nanocrystals^{119,120}. For example, Pt cuboctahedrons with (111) and (100) exposed surfaces and a size of 13 nm are capable of catalyzing the transformation of benzene to both cyclohexane and cyclohexene, while only the cyclohexane product is obtained when the morphology of Pt is a cube covered by the (100) surface¹²¹. Similar correlations between the catalytic activity/selectivity and morphology, i.e., the type of the nanocrystal's exposed surface, have also been observed in many other systems¹²²⁻¹²⁴. These and many other examples clearly illustrate the critical importance of the morphology control to the effective use of materials in a wide variety of applications.

CONCEPT OF SURFACE ENERGY

The seminal studies of Gibbs and Curie in the late 19th century¹²⁵, and later the application of the well-known Wulff rule, obtained the thermodynamic equilibrium shape and morphology of bare polyhedral crystals with size-independent surface energies^{126,127}. Over the last two decades, first-principle calculations based on the Wulff construction have been employed to provide atomistic models of the equilibrium morphologies for micro- and nano-materials *in vacuum*, liquid, and gas environments¹²⁸⁻¹³⁵. The morphology of micro- and nano-materials describes the set of crystallographic planes that appears at the exposed crystal surfaces.

The surface energy is perhaps the most fundamental characteristic of any material and helps in determining the trends of growth rate, surface segregation, and catalytic activity. Generally, crystals grow with the most stable surfaces, and are composed of surfaces with the lowest surface energy, which is high if the crystal facet consists of many kink atoms within the high index planes. Therefore, it is very difficult to grow high index facets in crystals. However, the experimental determination of surface energy is still rather difficult. For nanoparticles in particular, the strong size effect of the surface energy emerges when the particle diameter is less than a few nanometers. However, owing to the small size of nanoparticles, it is very difficult to measure the surface energy experimentally¹³⁶. Therefore, theoretical models and computer simulations must be developed to investigate the surface energy at the nanoscale. Because of the Wulff construction, the equilibrium morphology of a given material can be obtained using *ab initio* calculations^{131-134,137-142}. The procedure to obtain the complete set of morphologies, based on the Wulff construction and the surface energy, has been previously presented and employed as guide to match with experimental morphologies obtained for different binary oxides such as: Co_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, and In_2O_3 ¹³², as well as metals and metal oxides such as: Ag, anatase TiO_2 , and $\alpha\text{-Ag}_2\text{WO}_4$ ¹³¹, and *t*- LaVO_4 ¹³³, BaWO_4 ¹³⁷, ZnWO_4 ⁷⁵, BaMoO_4 ¹⁴³, CaMoO_4 ¹⁴⁴ and $\alpha\text{-AgVO}_3$ ⁸⁰. Then, we can apply our methodology to develop a consistent and reliable set of models for the morphology and corresponding exposed material surfaces.

Origami is the Japanese word for paper folding and refers to an ancient folding technique that transforms a flat sheet

into a complex three-dimensional (3D) shape. There exists a variation of origami called kirigami, which involves both cutting and folding. Origami and kirigami based design principles have recently attracted a growing amount of interest from the scientific and engineering communities, and have enabled a wide variety of promising applications such as self-assembling robots, reconfigurable mechanical metamaterials, self-deployable heart stents, dynamic solar tracking, flexible lithium-ion batteries, and soft actuators¹⁴⁵⁻¹⁵². Even, at biological level, the invention of DNA origami has deepened the understanding of how molecules could interact with each other in a complex self-assembly process and has accelerated the engineering of molecular systems with custom-designed structures and programmable behaviors¹⁵³⁻¹⁵⁹. In solid state, the concept of crystal origami has been introduced toward the rational design of surface structures of micro- and nano-crystallites^{144,160,161}.

The crucial step in semiconductor modeling involves the selection of an approach to ward approximating and describing the system's structural arrangement. Recently, our research group¹³¹ proposed an adequate methodology based on the Wulff construction for obtaining the available morphologies of a given crystal. This tool is useful in gaining a further understanding of how to achieve the morphological control of 3D nanocrystals by tuning the ratio of the surface energy values of the different facets. Additionally, we can predict the reaction pathway along the synthetic route and the experimental conditions that are crucial in obtaining the final material morphology and the corresponding properties. Therefore, the modifications of the synthetic route toward forming the determinate morphology are based on the same idea of manipulating a flat sheet in an origami- and kirigami-based design.

CORRELATING MORPHOLOGY AND PHOTOCATALYTIC ACTIVITY

Yan et al.¹⁶² have demonstrated the importance of determining the correlation between the morphology and the determined property in the fabrication and design of nanostructure inorganic semiconductor photocatalysts. Ng and Fan¹⁶⁰ have obtained different morphologies for the $\beta\text{-Ag}_2\text{MoO}_4$ crystal under different experimental conditions, and analyzed the photocatalytic activity of these morphologies using the degradation of Rhodamine B (RhB) under visible light irradiation. The authors demonstrated that the surface of the morphology plays an important role in the photocatalytic activity. Moreover, low-index facets exhibit low degradation rates, whereas high-index facets exhibit much higher degradation rates. In a previous study, our research group¹⁶³ obtained a different morphology for $\alpha\text{-Ag}_2\text{WO}_4$ synthesized with the chemical substitution of Ag by Ni atoms using the microwave-assisted hydrothermal method. The presence of Ni atoms on the $\alpha\text{-Ag}_2\text{WO}_4$ structure is responsible for the morphology variation, and thus for the variation of the photoluminescence emission profile. Yan and et al.¹⁶² have synthesized four typical orthorhombic Bi_2WO_6 nanostructures using the soluble inorganic-salt-assisted hydrothermal method, and analyzed their photocatalytic tetracycline degradation. In this case, the samples exhibited a morphology-dependent photocatalytic activity, and the deg-

radiation rate values for the 3D nanostructure were higher than those of the 2D nanostructure. The theoretical calculations can make good predictions for these values, which can in turn provide the information required to clarify the photocatalytic mechanism.

ZINC TUNGSTATE (ZnWO_4)

Recently, ternary-tungstate-based complex oxides have attracted the attention of researchers as potential candidates for efficient photocatalytic applications, including energy conversion and environmental purification, owing to their striking features such as low cost, environmental efficiency, and high stability under acidic and oxidative conditions¹⁶⁴⁻¹⁶⁷. As a representative member of this group, zinc tungstate (ZnWO_4) has received considerable attention, owing to its high thermal stability, excellent optical and electrical properties, and wide range of applications from photocatalytic, photoluminescent, to Li-battery anode materials¹⁶⁸⁻¹⁷¹. These ZnWO_4 characteristics result from its relatively high valence band and wide band gap^{172,173}, which can generate $\text{OH}\cdot$ with a strong oxidizing property to inactivate bacteria¹⁷⁴.

Therefore, ZnWO_4 is an ideal photocatalyst for inactivating *Macrocyctis pyrifera* by an integrated $\text{OH}\cdot$ and hot water pretreatment^{175,176}. With regard to microorganisms, ZnWO_4 has a wide application prospect, owing to its bactericidal effects resulting from the high oxygen evolution potential^{177,178}, wherein the generated $\text{OH}\cdot$ has a stronger oxidation ability than TiO_2 ^{170,179}.

Understanding the complicated relationship between various synthetic processing parameters and the functional properties or performance of nanoparticles is one of the objectives in the computational design of materials, and an ideal problem in materials informatics. In clarifying the complex relationship between various synthetic processing parameters, such as temperature, growth rates (moderated by precursors and surfactants), and time, the final functional properties or the performance are the objectives of the computational design of materials, particularly in the engineering of photocatalysts, in addition to being an ideal problem in materials science. The motivation for this study was provided from our previous studies on ZnWO_4 ⁷⁵. Here, we present our investigation to ward clarifying its photocatalytic activity. Additionally, this study seeks to fulfill a three-fold objective. First, on the basis of the first-principle density function theory (DFT), we investigate the (001), (010), (100), (110), (101), (011), and (111) low-index exposed surfaces of ZnWO_4 to clarify their morphology, geometry, and electronic structures. Secondly, in an attempt to illuminate the relationship between the morphology and photocatalytic activity of ZnWO_4 , we must understand the morphology changes as a function of the relative stability of surfaces. Thirdly, we obtain new clues for understanding the atomic properties and morphology of the ZnWO_4 microcrystal and its contribution toward improving the efficiency of the photocatalytic process. Then, the relevant mechanisms are investigated through calculations from first-principles to provide new insight into the high photocatalytic activity of ZnWO_4 based on the analysis of the local under-coordination of both Zn and W cations in the exposed surfaces covered by the morphology. To this end, the

role of the exposed surfaces on the photoactivity of ZnWO_4 , and particularly the geometry and electronic structure of the incomplete clusters of both Zn and W cations, are elucidated using the Kröger-Vink notation and by analyzing the number of the Zn–O and W–O breaking bonds in these clusters, i.e., the under-coordinated clusters. Thus, we are able to identify that these clusters are the main contributors to the photocatalytic process, which can help us clarify their mechanism.

ZnWO_4 BULK AND SURFACE STRUCTURES

Our group has previously presented the synthesis of ZnWO_4 nanocrystals⁶⁷ using the microwave hydrothermal method (HM) at three different temperatures (140 °C, 150 °C and 160 °C). These nanocrystals had a wolframite structure within the monoclinic $P2/c$ ^{177,180-183} space group. The building blocks of the ZnWO_4 structure were the distorted octahedra of the $[\text{ZnO}_6]$ and $[\text{WO}_6]$ clusters, which generated structural defects in the lattice, as shown in **Figure 2**.

The results revealed that the different efficiency of the photocatalytic properties was caused by the preferential orientated growth and this orientation is the specific surface in the growth process, as shown in the transmission electronic microscopy (TEM and HR-TEM) images shown

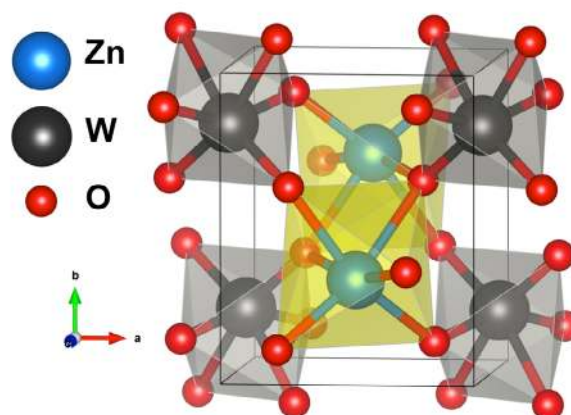


Figure 2. Unit cell representation of monoclinic ZnWO_4 structure and octahedral $[\text{ZnO}_6]$ and $[\text{WO}_6]$ clusters.

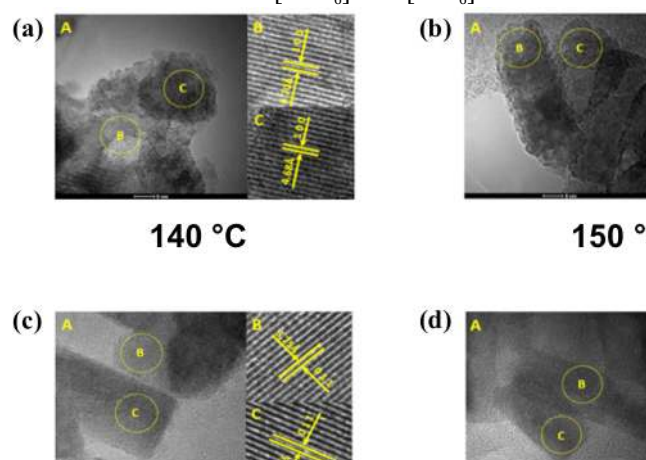


Figure 3. Images of ZnWO_4 nanocrystals obtained by Pereira et al. using MH method at: (a) 140 °C: A-TEM, B, and C-HR-TEM; (b) 150 °C: A-TEM, B, and C-HR-TEM; (c) and (d) 160 °C: A-TEM, B, and C-HR-TEM. Reproduced from Ref. 75 with permission from The Royal Society of Chemistry.

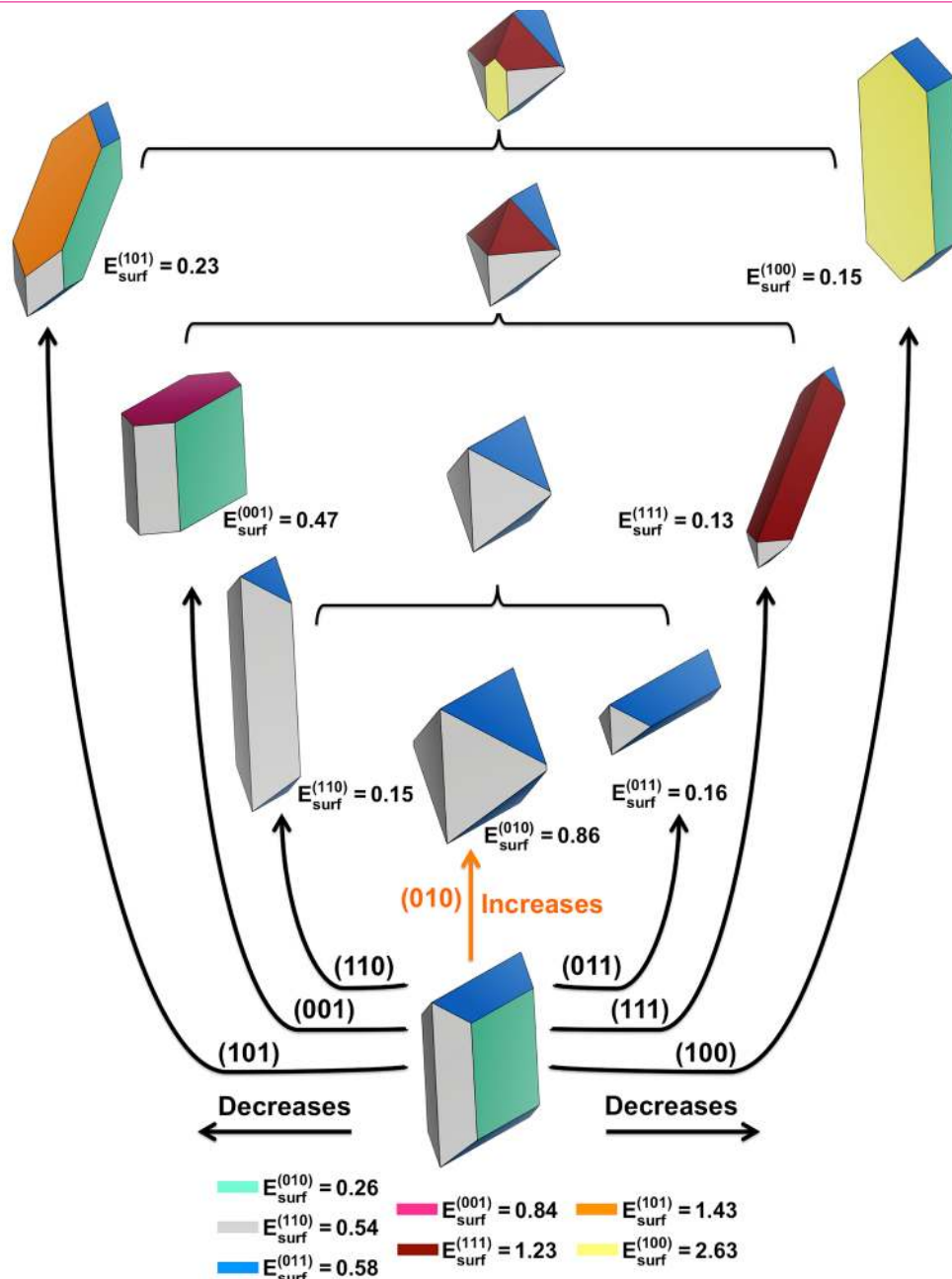


Figure 4. Available morphologies of monoclinic ZnWO₄ structure. Surface energy (E_{surf}) is in Jm^{-2} .

in **Figure 3**.

Understanding the correct surface and surface composition is crucial for their photocatalytic application. To this end, ZnWO₄ can be cleaved in various possible crystallographic planes. First, we present the available morphologies of ZnWO₄, based on the Wulff construction and the surface energy values calculated for the (001), (010), (100), (110), (101), (011), and (111) surfaces shown in **Figure 4**.

WHAT MAKES THE DIFFERENCE?

The most important information from **Figure 4** is the presence of the (011) and (010) surfaces in all of the available ZnWO₄ morphologies, and the invariant properties involved in their photocatalytic activity⁷⁵.

The TEM and HR-TEM images at different temperatures (140 °C, 150 °C, and 160 °C) in the synthesis (**Figure 3**) show that the growth mechanism is controlled by the direction of the more stable surfaces in the order of (100) >

(111) > (011) > (010), which can be associated to the experimental MH method used in the synthesis.

The particular crystal orientations lead to differences in the number of broken bonds at each exposed surface, i.e., the anisotropic surface broken bonds¹⁸⁴, which are known as the anisotropic surface reactivity^{185,186}. By carefully analyzing the atomic arrangement of the atoms after the optimization process, it is possible to calculate the broken bond density (D_b) and observe which clusters are present at the top of each surface. The D_b calculation was proposed by Gao et al.^{184,187,188} and is the ratio between the number of broken bonds (N_b) per area (A) for each surface. **Table 1** lists the surface energy values⁷⁵ and the broken bond density. Generally, the D_b values are directly linked to the order of the surface energy stability, i.e., higher values of D_b represent a large quantity of defects on the surface and also a higher surface energy value.

Table 1. Values of surface area, broken bond number,

broken bond density, and surface energy for each ZnWO₄ surface.

Surface	Surface area (nm ²)	Broken bond number (N _b)	Broken bond density (D _b , nm ⁻²)	Surface energy (Jm ⁻²)
(010)	0.236	4	16.95	0.26
(110)	0.374	8	21.39	0.54
(011)	0.364	6	16.48	0.58
(001)	0.277	6	21.66	0.84
(111)	0.466	12	25.75	1.23
(101)	0.402	8	19.90	1.43
(100)	0.290	8	27.59	2.63

The analysis of the results presented in **Table 1** shows that the (010) surface has the lower value of surface energy (0.26 Jm⁻²) with the lowest value of the broken bond number (N_b = 4). The (110) and (011) surfaces have similar surface energy values, i.e., 0.54 and 0.58 Jm⁻², with different

values of N_b = 8 and 6, respectively. Moreover, the (001), (111), (101) and (100) surfaces display the following order of stability: 0.84 < 1.23 < 1.43 < 2.63 Jm⁻², respectively, with N_b = 6, 12, 8, and 8, respectively. Therefore, in this case, there does not exist a correlation between the surface stability and the N_b or broken bond density D_b.

Hence, we must find a way to correlate the photocatalytic activity of ZnWO₄ with the presence of the different exposed faces in the morphology, independently of the N_b and D_b values. To this end, we provide the theoretical/computational foundation for the analysis of their electronic properties. **Figure 5** illustrates the clusters present in all investigated surfaces for the monoclinic ZnWO₄ material. From the analysis of the top of each surface, it is observed that not only the under-coordinated atoms (clusters) are involved in the surfaces, but they are also involved in the distorted clusters. In any case, the crystal shape of interest and this crystal shape depend on the surface structure.

Using the Kröger-Vink notation¹⁸⁹, the oxygen vacancies

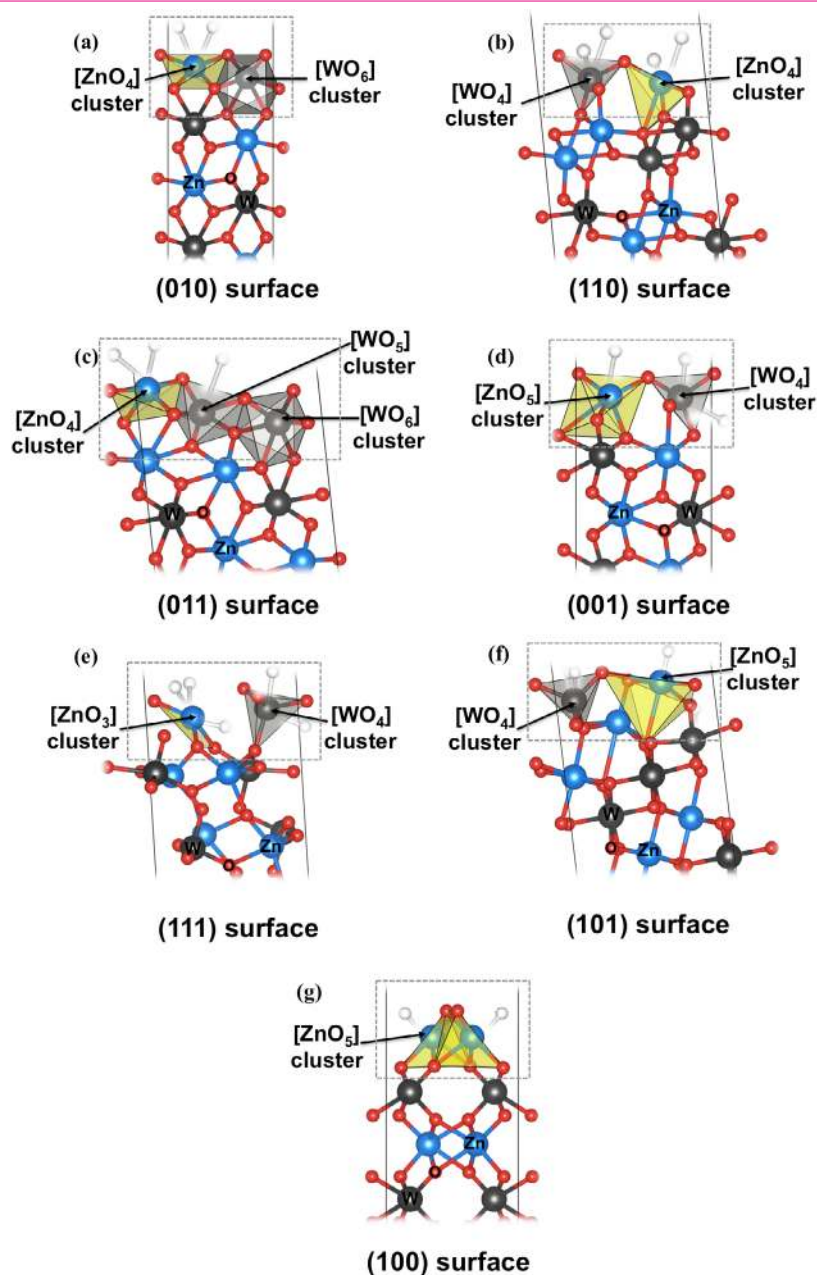


Figure 5. Surface models for monoclinic ZnWO₄ structure: (a) (010), (b) (110), (c) (011), (d) (001), (e) (111), (f) (101), and (g) (100) surfaces. The clusters at the top of each surface are highlighted.

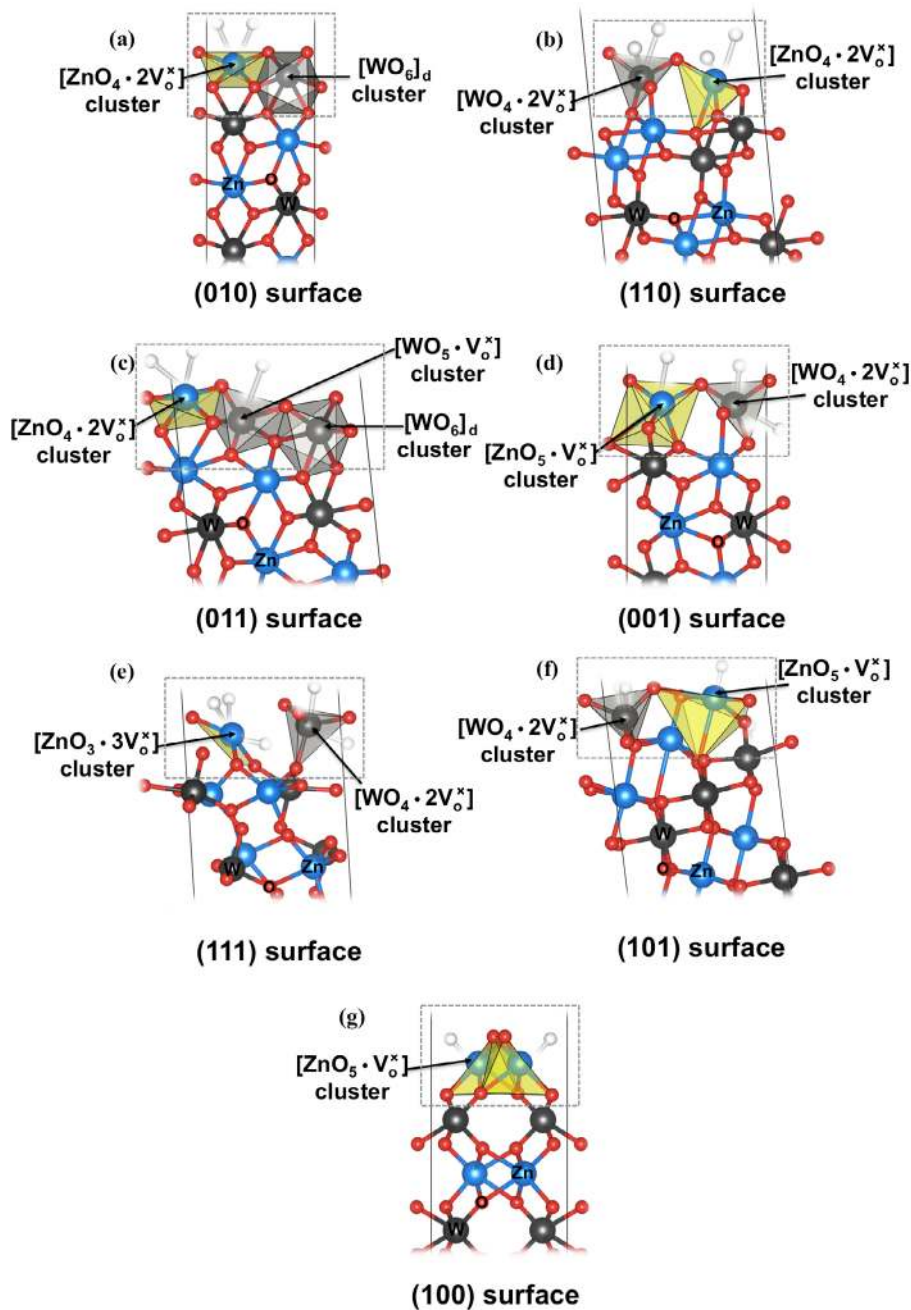


Figure 6. Surface models for monoclinic ZnWO₄ structure: (a) (010), (b) (110), (c) (011), (d) (001), (e) (111), (f) (101), and (g) (100) surfaces, where V_O^x denotes neutral oxygen vacancy and []_d denotes distorted cluster.

can be written as V_O^x and has with a neutral charge. Therefore, the superficial clusters can be written as: [MO₄·2V_O^x], [MO₄·2V_O^x], where M=Zn and W, and [ZnO₃·3V_O^x]. At the top of the (010) and (011) surfaces, there exist structural and distorted octahedral clusters called [WO₆]_d, as shown in **Figure 6**.

ELECTRONIC STRUCTURES AND PHOTOCATALYTIC MECHANISM

The physicochemical properties of materials are the manifestation of their electronic structure. In particular, the electronic band structure involving the valence position and the conduction band edges, and the Fermi level that can be tuned as a function of the morphology and composition of the materials. The Fermi level is considered as the total chemical or electrochemical potential for electrons,

and its precise understanding is essential to relate the electronic band structure and the charge transfer characteristics in the materials¹⁹⁰. The electronic structure of the different exposed surfaces was analyzed by calculating the density-of-states (DOS) functions and the band gap value.

The photocatalysts' electronic band structure, which is responsible for the photocatalysts, can be tuned using the specific exposed surfaces, which has significant impact on the redox abilities of photoinduced carriers¹⁹¹. The DOS plots (total and projected on atoms) based on the DFT calculations for the (010), (110), (011), (001), (111), and (101) surfaces are shown in **Figure 7**.

ZnWO₄ has a calculated (direct) band gap of 3.85 eV, which is comparable to the experimental value⁷⁵. The analysis of the results revealed that the maximum VB is predominantly composed of the O 2p states while the CB minimum is predominantly composed of the W 5d states.

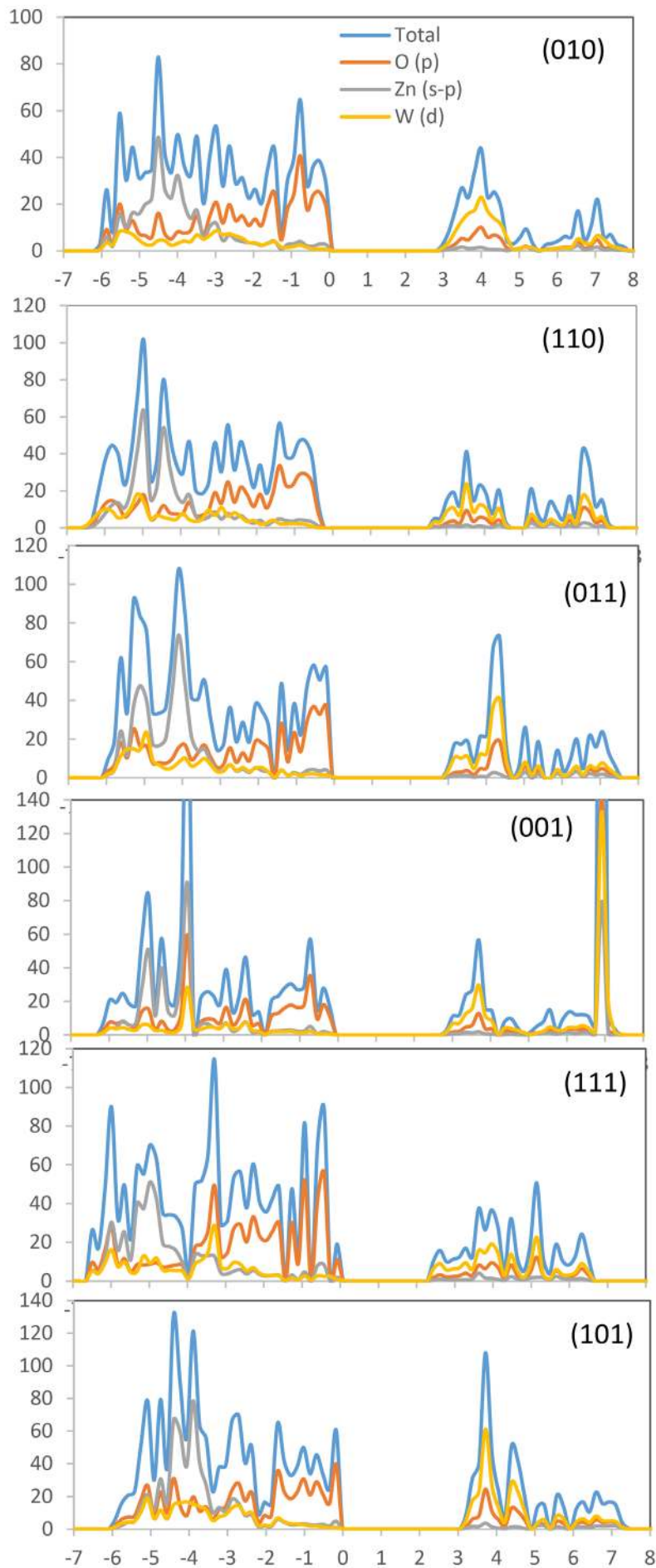


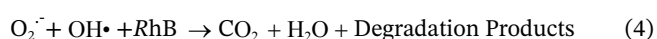
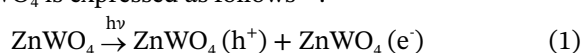
Figure 7. Density-of-states for (010), (110), (011), (001), (111), and (101) surfaces of ZnWO₄. Fermi level is set to zero.

Additionally, the figures show that the essential features of the different surfaces remain constant, but the more stable surfaces, i.e., (010), (110), and (011), exhibit a similar split-off feature in the O 2*p* and W 5*d* partial DOS at the top of VB and bottom of CB, where the transfer of electrons is produced to generate the e⁻/h⁺ pairs.

The lack of reliable models that can describe the photocatalytic process is one of the biggest challenges toward achieving the long-term goal of optimizing the photocatalytic activity. The underlying mechanism is still heavily debated, but our proposed photocatalytic degradation mechanism, which is based on a comprehensive literature review^{101,192-194} and the results of this study, is as follows: the first step is the absorption of light with energy equal to or greater than the band gap energy of the material. Consequently, the photon absorption causes the transfer of electrons (e⁻) from the VB to the CB and the subsequent generation of holes (h⁺) in the VB¹⁹⁵. As shown in previous studies on ZnWO₄⁵⁸, electronic structure and polaron formation can provide crucial information on the electronic properties of complex transition-metal oxides¹⁹⁶. In this context, Hoang et al.⁵⁸ have shown that the electron polaron associated with the reduction of W⁶⁺ to W⁵⁺ is thus not stable in ZnWO₄, that can be associated to their electronic structure in which there is a strong mixing between the Zn 3*d* and W 5*d* states at the CB maximum. As a result, an electron when added to the materials along the reduction process cannot be localized on any particular W cation and then the hole polaron, i.e. electron/hole (e⁻/h⁺) pairs are not formed and ZnWO₄ are not active when used as pseudocapacitive electrode materials¹⁹⁷.

The electrons in the CB and the holes in the VB exhibit high reducing and oxidizing power, respectively, and the migration of these charge-carriers (e⁻/h⁺) to the surface leads to oxidation. Additionally, the reduction reactions produce hydroxyl (OH•) and superoxide (O₂^{•-}) radicals, respectively. The electron can react with molecular oxygen to produce superoxide anions (O₂^{•-}) through a reductive process. The hole can abstract electrons from water and/or hydroxyl ions to generate hydroxyl radicals (OH•) through an oxidative process¹⁹⁸. Singlet oxygen (¹O₂) is mostly produced indirectly from the aqueous reactions of O₂^{•-}¹⁹⁵. Moreover, OH• is a strong and non-selective oxidant that can damage virtually all types of organic biomolecules¹⁹⁹. It is important to note that ¹O₂ is the main mediator of photocytotoxicity; it can irreversibly damage the treated tissues, and thus induce the oxidation and degradation of the biomembrane^{200,201}. Moreover, as a precursor of OH• and ¹O₂, O₂^{•-} is not a strong oxidant, although it plays a key role in the biological activity²⁰².

The photocatalytic oxidization activities were evaluated by RhB degradation. Generally, the main oxidizing species were OH• and O₂^{•-} radicals²⁰³⁻²⁰⁵. The standard mechanism proposed by Zhang et al. for the photocatalytic reaction of the ZnWO₄ is expressed as follows¹⁷⁰:

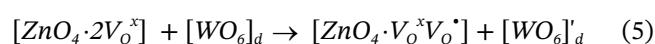


Although many previous studies have investigated the photocatalytic mechanism, to the best of our knowledge, few studies have investigated the role of geometry and the electronic properties of the distorted octahedral [ZnO₄] and [WO₆] clusters at the exposed surfaces¹⁷³ in the morphology (e.g., the under-coordination of both the Zn and W cations and electronic charge) during the ROS generation from H₂O and O₂. A deeper understanding of this aspect will allow us to interpret the underlying ROS generation mechanisms, potentially predict the amount of ROS generation or the photocatalytic activity of newly synthesized ZnWO₄, and effectively reduce the costs of experimental testing.

A further challenge regards the very complicated electronic structures of the encountered ZnWO₄, as is vividly illustrated by its naked exposed surfaces. To clarify the crucial factors affecting performance, a computational investigation was conducted to determine the relationship between the exposed clusters and the photocatalytic activity. To clarify the crucial factor affecting this correlation, the analysis of **Figure 5**, in particular the active (010) and (011) surfaces, elucidated the cause for the presence of [ZnO₄] and [WO₆] in at surface (010), and for the presence of [ZnO₄], [WO₅], and [WO₆] at surface (011). The clusters were similar when the Kröger-Vink notation was used, and expressed as: [ZnO₄] ≡ [ZnO₄·2V_O^x], [WO₅] ≡ [WO₅·V_O^x] and [WO₆] ≡ [WO₆]_d (**Figure 6**).

By examining **Figure 6**, it can be observed that there existed oxygen vacancies related with both the W and the Zn clusters. However, it should be emphasized that the W clusters formed the network because they were more stable. This stability resulted from the covalent nature of the W-O bonds. Thus, in the formation of the electron/hole pairs that can be associated to a charge separation process with the concomitant formation of dipoles, the W clusters [WO₆]_d acted as electron receptors. Thus, the oxygen vacancies formed in the Zn clusters [ZnO₄·2V_O^x] or W clusters [WO₅·V_O^x], and were capable of transferring electrons to the tungsten clusters [WO₆]_d, and thus form permanent dipoles. Surfaces (010) and (011) were the most active in the photodegradation, owing to the appearance of these W and Zn clusters and the oxygen vacancies, which generated stable quantum dots. Thus, they were more likely to transfer the electron/hole to O₂ and H₂O, respectively. In **Table 1**, these surfaces are those with a smaller D_b and different surface energies.

These two surfaces were unique surfaces amongst all of the low-index surfaces of the monoclinic ZnWO₄ structure with both types of clusters at the top of the surface, as shown in **Figure 6**. In the lattice and superficial framework of the ZnWO₄, there existed a cluster-to-cluster charge transfer process, which generated the electron/hole pair responsible for the photocatalytic process. At the (010) exposed surface, these electronic rearrangements occurred from [ZnO₄·2V_O^x] to [WO₆]_d and formed a negatively charged cluster [WO₆]_d⁻, and a positively charged cluster [ZnO₄·V_O^xV_O^x], i.e., an electronic charge separation, as follows:



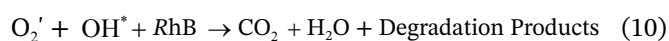
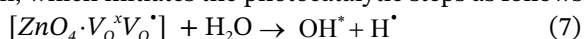
For the exposed (011) surface, the charge transfer process occurred from to:



where superscript (x) indicates a neutral charge, symbol (\bullet) corresponds to a positive charge, and a negative charge is denoted by symbol ($'$)²⁰⁶, using the Kröger-Vink notation¹⁸⁹.

Based on the analysis of the geometry and electronic properties for the exposed surface clusters, we hypothesize a detailed mechanism, wherein the structure-function relationship is clarified at the atomic level, in consistency with the DFT calculations presented above.

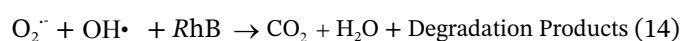
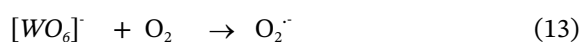
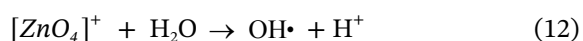
Therefore, along the photocatalytic mechanism, the H₂O can react with the $[ZnO_4 \cdot V_O^x V_O^\bullet]$ and/or $[WO_5 \cdot V_O^\bullet]$ cluster, while the O₂ can react with the $[WO_6]_d'$ cluster. In other words, the $[ZnO_4 \cdot V_O^x V_O^\bullet]$ and/or $[WO_5 \cdot V_O^\bullet]$ cluster are the sources of the holes, while the $[WO_6]_d'$ cluster supplies the electron, which initiates the photocatalytic steps as follows:



The proposed mechanism for the photocatalytic reaction can also be expressed using the concept of the clusters appearing at the exposed surfaces, as an alternative to the standard mechanism proposed by Zhang et al.¹⁷⁰, as follows:



This step corresponds to the symmetry breaking process associated with an electronic charge transfer with a concomitant formation of positive $[ZnO_4]^+$, and negative $[WO_6]^-$, centers that can be described with the formation of h^+ and e^- , i.e., charge-carriers (e^-/h^+), respectively. Considering the DOS analysis (Figure 7), we can conclude that the charge transfer process occurs from the 5d and 3d orbitals of both the W $[WO_6]$, and the Zn $[ZnO_4]$, centers at CB, respectively, to the 2p orbital of the O anions at the VB. Then, h^+ and e^- act as h^+ and e^- , respectively, as follows:



It is important to note that the remaining exposed surfaces do not exhibit under-coordinated clusters that are capable of generating electrons and holes with a tungstate cluster, i.e., an electron/hole pair, and thus prevent its participation in the photocatalytic mechanism. In summary, the presence of both the (010) and (011) surfaces in the morphology is a necessary condition for the ZnWO₄ material to act as a photocatalyst, because only these exposed surfaces enable the presence of $[ZnO_4 \cdot 2V_O^x]$ (at the (010) surface) and $[WO_5 \cdot V_O^x]$ (at the (011) surface) to act as electron donors to the adjacent $[WO_6]_d$ clusters. This electronic charge process induces the formation of an electron/hole pair, wherein the $[ZnO_4 \cdot V_O^x V_O^\bullet]/[WO_5 \cdot V_O^\bullet]$ and $[WO_6]_d'$ clusters are the active sites capable of reacting with H₂O and O₂, respectively, to initiate the photocatalytic mechanism.

CONCLUSIONS AND OUTLOOK

Chemical ordering, i.e., the arrangement of different species within a material, along with the size, morphology, and average composition, has a profound influence on optical, catalytic, and numerous other properties. In particular, research into controlling the morphology of micro- and nano-crystals is highly relevant to fields as diverse as materials science, catalysis, chemistry of materials, and nanotechnology. Computational studies provide an alternative approach to ward improving our fundamental understanding of solid morphologies and predicting the properties of novel materials with unusual exposed surfaces. Tuning the surface structure at the atomic level is of primary importance to simultaneously satisfy the catalytic performance and stability criteria required for the development of photocatalysts.

A comprehensive understanding of the origins of photocatalytic activity is often very difficult, and relies heavily on Edisonian trial-and-error processes, which lack adherence to theoretical and systematical guidelines and require the inclusion of other relevant factors. To this end, we attempt to address this question by applying density functional theory (DFT) simulations, and by verifying the results obtained from experimental data. Here, we present a consistent study on the structural, chemical and electronic properties of exposed ZnWO₄ surfaces. The available morphologies of the materials are found using first-principle calculations, based on the Wulff constructions. Additionally, we explicitly unveil the exposed surfaces as a key factor that defines the photoactivity of ZnWO₄.

As a proof of concept, the experimentally unknown key role of the structure and the electronic properties of the clusters, i.e., the local coordination of both the Zn and W cations located at the exposed surface, are highlighted. We report atomic details to clarify the influence of different exposed surfaces on the catalytic mechanism, which provides an atomic-level understanding of the geometric and electronic structures of their surfaces to comprehend, predict, and explain how catalytic properties emerge. The reliability of the proposed theoretical model was verified. Our simulations revealed that there exist two important factors that must be considered when investigating the surface electronic properties of ZnWO₄. First, the (010) and (011) surfaces appear in all of the available morphologies with enhanced photocatalytic activity. The second factor is the specific local environment surrounding the site of interest, i.e., the cluster at the exposed surface. We found that the stability of the surfaces and their electronic properties are correlated with the presence of $[ZnO_4 \cdot 2V_O^x]$, $[WO_5 \cdot V_O^x]$, and $[WO_6]_d$ clusters, and that reservoirs of electrons and holes, respectively, are active sites in the photocatalytic process. The structure-function correlation between the electronic properties and the morphology was investigated for ZnWO₄.

The main conclusion drawn from this study is that both the intrinsic atomic properties and the electronic structure of the incomplete surface clusters, which appear at the exposed surfaces of the morphology, are required to explain the photocatalytic activity. These results indicate that the intrinsic atomic properties of metal oxide are controlled by the surface clusters present in the morphology. By computing the exposed surfaces and the available morphologies, we extracted an image of the effects exerted by the varying surface energy on

the stability, morphology, and position of the Fermi level. We demonstrated that the morphological variations can induce significant changes in the electronic properties, and their relevance in various experimental manifestations. DFT links the latter phenomena to the structural and electronic disorder of under-coordinated clusters for both the Zn and W cations, which mimic an atomic recognition pattern that allows the identification of the local structure of active sites and the enhancement of catalytic performance. This study introduces a new approach toward thinking about ZnWO₄ morphology, and provides a deep understanding of the relationship between the atomic structure and the electronic properties with regard to catalyst design.

Overall, the precise control of active sites on the exposed surfaces developed in this study represents a key step toward rational catalyst design, and provides a novel way of thinking that can be extrapolated to other semiconductors. For experimentalists, precise control with the on-demand manipulation of semiconductor morphology is of extreme interest. Ultimately, the bright future of semiconductors hinges upon the ability of the computational community to move from rationalizing to predicting materials, and the willingness of experimental researchers to take the resulting design principles on board. Our study provides fundamental and practical insights into the role of the surface structure and highlights strategies of designing more efficient photocatalysts. The predictive modeling approach proposed in this paper is general; therefore, it can be applied to other semiconductor structures and contribute to better-engineered materials in photocatalytic applications.

The process of photocatalysis involves the excitation of materials with the creation of electrons and holes, which points to the increasingly prominent role of electronic states other than the fundamental state. Therefore, work is in progress with regard to the modelling of electronic excited states for different exposed surfaces. The results of the ongoing investigations will be reported in the near future.

For future research in this field, to figure out exactly how molecules, in particular O₂, H₂O and ¹O₂, and radicals, OH• and O₂^{•-}, interact with surfaces and with each other on diverse surfaces environment is still challenging, and a synergetic study including both experiment and theory is of critical importance. First, in order to characterize the intermediate states, more effort should focus on the surface local-structure analysis before and after the surface chemical reaction, and moreover the development of higher temporal and energy resolution techniques for *in-situ* characterization of surface process is also needed. Second, based on structural analysis and *in-situ* measurement, a more quantitative quantum chemistry model beyond qualitative phenomenological model is hope to be developed. On this basis, a more precision and systematic surface chemical engineering strategy is expected. Third, as a remarkable outcome, the understanding that has been built on the structure-properties relationship would enable improved reliable stability and repeatability of surface chemistry modification, which are critical for promoting promising applications, and we are confident that, with the development of surface chemistry modulation, new breakthroughs in basic science.

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Notes

The authors declare no competing financial interest.

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