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1 X-ray spectroscopies studies of the 3d transition

2 metal oxides and the applications on

3 photocatalysis

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11 Abstract:

12 Recent advances in synchrotron based X-ray spectroscopy enable materials scientists
13 to emanate finger prints on important materials properties e.g. *electronic*, *optical*,
14 *structural* and *magnetic* properties, in real time and under nearly real-world
15 conditions. This characterization in combination with optimized materials synthesis
16 routes and tailored morphological properties could contribute greatly to the advances
17 in solid-state electronics and renewable energy technologies. In connection to this,
18 such perspective reflects the current materials research in the space of emerging
19 energy technologies, namely photocatalysis, with a focus on transition metal oxides
20 (TMOs), mainly on the Fe₂O₃ and TiO₂ based materials.

21 1. Introduction

22 In the quest to achieve carbon neutrality and reduce our overall footprints on the

environment is has become more crucial than ever before to realize new and sustainable green energy technologies including energy *generation, storage* and *transportation*.

Looking into emerging energy technologies from materials research perspective, photocatalysis, often referred as *artificial photosynthesis*, is the light-induced acceleration of a reaction in the presence of a light-sensitive catalyst, similar to how plants use chlorophyll to convert water and carbon dioxide into oxygen and glucose fueled by sunlight.¹ Artificial photosynthesis offers many exciting opportunities for large-scale production of hydrogen gas from water (Fig. 1) and decomposition of water borne pollutants.

As is evident in Figure 1 crucial challenges associated with photocatalysis include (i) band gap engineering of the light sensitive catalyst to optimize the photoelectric effect in the visible wavelength range, (ii) effective separation of photoelectrons and their associated holes preventing their recombination and (iii) alignment of the relative energy position of the catalyst to that of the reactant in order to discharge the same through a re-dox reaction facilitated by the photoelectrons and holes. Specifically for water splitting, to substantially photo-catalyze the reaction without applying external potential, the conduction band minimum (CBM) of the catalyst should be higher than the potential of dihydrogen evolution ($\text{H}_2/\text{H}_2\text{O}$): $\text{H}^+ \rightarrow \text{H}_2$ ca. 0 eV vs NHE (normal hydrogen electrode) while the valence band maximum (VBM) of the catalyst should be lower than the potential of dioxygen evolution ($\text{O}_2/\text{H}_2\text{O}$): $\text{O}^{2-} \rightarrow \text{O}_2$ ca. 1.23 eV vs NHE²⁻⁶ as indicated in Figure 1.

Reflecting over the myriad of available material complexes, metal oxide compounds at reduced scale, particularly 3d transition metal oxides (TMOs) have established their prominence in the field in light of their stability, cost efficiency and most importantly tunability of their electronic characteristics which scale with their morphological properties and chemical composition.⁷⁻¹⁶

The band structure of 3d TMOs is typically altered and optimized through self-construction i.e. alteration of their morphological (size/shape) and chemical properties (introduction of impurity elements into the host matrix substituting for either host cations and/or anions). Following recent progresses in material researches, we are not

Figure 1: The principle of water splitting on a semiconductor catalyst. The energy level scale is indicated in the figure using either the NHE or vacuum level as reference. The energy difference between the $E_{0, NHE}$ and $E_{0, vacuum}$ is 4.44 eV.

only able to synthesize nanoscale materials complexes with carefully altered and tailored properties with high reproducibility but also evaluate important materials properties at high precision both ex-situ and *in-situ/in-operando* down at atomic level with high precision to predict evolution and requirements *in* and *for* optimum performance..

We present herein an overview on synchrotron based X-ray spectroscopy and its implementation in materials development for energy application with focus on 3d TMOs. Specifically, this perspective is composed of following three parts:

(i) The first part of this paper provides a detailed description of the principles and capabilities of soft X-ray spectroscopies, including X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) as well as associated spectral features (ii) The second part of this paper describes the electronic structure of selected 3d TMOs and the evolution in the same upon alteration of their chemical composition and morphological properties. (iii) The third part of this paper reflects over recent development and advances in *in-situ/operando* spectroscopy technique that strengthens our efforts in developing new and sustainable green energy alternatives.

2. Application of synchrotron based soft X-ray spectroscopy in energy research

2.1 Principles of synchrotron spectroscopy

Synchrotron radiation refers to polarized light/radiation of high brilliance produced from charged particles (e.g. electrons) travelling at relativistic speed along a curved trajectory. Synchrotron spectroscopy is the utilization of synchrotron radiation to elucidate details of the electron structure and molecular dynamics in matter. XAS and

76XES are two principle spectroscopic capabilities employed for detailed projection of
 77the density of unoccupied and occupied states, respectively. Following excitation core
 78levels electrons into higher energy states enables chemical/elemental and orbital
 79selectivity. ¹⁶⁻²⁰

80XAS is recognized by the excitation of core electrons to the conduction bands,
 81governed by the dipole selection rule, which creates a vacancy at the core level that is
 82re-populated following a decay of the electrons in the occupied density of states. The
 83interaction between (soft) x-ray photons and condensed matter is so strong that
 84measureable intensity of the transmitted photon flux would require ultra-thin and
 85uniform sample slices, which is unrealistic for most of the materials of interest.

Figure 2: Principle of the transition process and simulated soft X-ray absorption spectrum of selected 3d TM reflecting their typical L-edge spectral features and K-edge spectral features of oxygen.

86Instead of direct recording the transmitted photon flux, the energy distribution as a
 87function of the altering excitation energy by recording the decay process is employed
 88to obtain an absorption spectrum. For a given element, different edges therein can be

selectively excited, depending on the excitation energy that provides accurate information on band-to-band and orbital transitions (Figure 2). Typically, XAS is recorded either in the bulk-sensitive total Fluorescence yield (TFY) detection mode by measuring the emitted photons with a photodetector or in the surface-sensitive total electron yield (TEY) detection mode by recording the surface drain current. The TFY and TEY signals reflect sample information of probing depth up to several hundred nanometers and tens nanometers, respectively.²¹

In contrast to XAS where the excitation energy is altered, in XES core electrons are excited at constant excitation energy and the emission is recorded (using a grating spectrometer wherein the intensity distribution as a function of photon energy) as core holes are re-populated by electrons in the occupied density of states. Following the decay route of valence electrons in the emission process, the detection depth of XES is hundred nanometers, as compared to few of nanometers in the case of XAS. Furthermore, emission spectroscopy is categorized in two techniques depending on whether core electrons are excited at energies far beyond the absorption edge a.k.a. normal X-ray emission (nr-XES) or at energies tuned to the absorption spectral features a.k.a. resonant inelastic X-ray scattering (RIXS). While nr-XES describes the

Figure 3: The schematic band level diagram of RIXS process of the 3d TMOs.

total density of occupied states, RIXS relates to the eigenvalues of the ground states through the intermediate states. Figure 3 presents the typical energy level diagram of a TMO where the spin-orbital splitting on the 2p and 3d has been simplified (L refers to the ligand – O and $3d^{n+1}$ is the electron transfer from ligand to TM cation)²². Excitation of a valence electron at $3d^n$ to $3d^{n+1}$ intermediate state gives rise to electron decay to the ground state and $3d^{n+1}L^{-1}$ and $3d^n$, giving rise to both energy loss (inelastic peaks) and zero energy loss (elastic peak) spectral features.

2.2 Typical spectral features of 3d TMOs

TiO_2 and Fe_2O_3 are amongst the most widely studied photoelectric materials complexes and two promising TMOs for photoelectric applications (particularly photocatalysis) in light of their readily tunable electronic properties and inherent chemical stability, biocompatibility, zero toxicity and availability at low production cost.¹⁶ In the following sections of this we will discuss the electronic properties of intrinsic TiO_2 and Fe_2O_3 and the evolution in the same upon alternation of their chemical composition and morphological properties by reflecting over their respective XAS and XES spectral features.

2.2.1 XAS spectral features of 3d TMOs

The absorption spectral features at the L-edge (L_2 and L_3) of TMs arise from $2p_{1/2}$ and $2p_{3/2}$ core levels, respectively, following spin-orbital coupling. The Ti L-edge of TiO_2

Figure 4: (a) Ti L-edge XAS of TiO_2 and Fe L-edge XAS of Fe_2O_3 , (b) O K-edge XAS of TiO_2 , MnO_2 , Fe_2O_3 and NiO , (c) variation in 3d-4sp band intensity ratio as a function of the number of electrons in the TM 3d state, references of TiO_2 , MnO_2 , Fe_2O_3 and NiO , were applied to obtain the plot.

and Fe L-edge XAS of Fe_2O_3 have been displayed in the Figure 4 (a). In the case of TiO_2 , the L_3 and L_2 peaks arise from Ti $2p_{3/2}$ and $2p_{1/2}$ core transitions to unoccupied Ti

127 $3d_{5/2}$ and $3d_{3/2}$ states and are typically observed in the energy range 458-462 eV and
128 462-468 eV, respectively. As shown for spectra of both TiO_2 and Fe_2O_3 , the $L_{2,3}$ edges
129 further split to the t_{2g} and e_g peaks following the crystal field splitting which originates
130 from the electrostatic field following repulsive interaction between 3d TMs cations
131 and O anions.²³ While e_g orbital points towards the O site, which aligns with the
132 electrostatic field orientation, t_{2g} orbital points between O sites. A stronger crystal
133 field effect on the e_g orbital results in a shift of e_g towards higher energies further away
134 from t_{2g} . In absorption spectra, the energy separation between e_g and t_{2g} represents the
135 crystal field strength.²⁴⁻²⁶

136 If we consider TiO_2 , the O K-edge XAS of the TMO reflects O 1s excitation to
137 unoccupied O 2p states, O 2p-Ti 3d and O 2p-Ti 4sp hybridization.²³ These features
138 are typically grouped into two regions, *below* and *above* the ionization threshold
139 recognized by (i) O 2p-Ti 3d (in the energy range 530-536 eV) and (ii) O 2p-Ti 4sp
140 and O 2p (in the energy range 536-550 eV). Similar to the Ti L-edge XAS, the crystal
141 field splitting of the 2p-3d hybridization is observed at ca. 530-536 eV in the O K-
142 edge XAS. Figure 4 (b) presents the XAS of few selected TMOs wherein the crystal
143 field splitting varies depending on the electronic configuration of the TMO. While
144 most 3d TMOs show similar O K-edge spectral profile, the same for ZnO deviates due
145 to the $3d^{10}$ configuration of the Zn cation which results in the absence of O 2p-Zn 3d
146 hybridization feature.⁹

147 The relative ratio between the spectral features above and below the ionization
148 threshold relates to the number of partially unoccupied TM 3d states available for

149 hybridization with unoccupied O 2p states. Upon plotting the band intensity ratio of
 150 the region below/above the ionization threshold against the 3d electrons numbers, the
 151 O K-edge XAS across the 3d TMOs in Figure 4 (b) can be quantitatively analyzed
 152 (Figure 4 (c)). Furthermore, with shrinking of the metal 3d orbitals in the late 3d
 153 TMOs diminishes the p-d hybridization effects, leading to the termination of the linear
 154 interpolation at d^9 instead of d^{10} .²⁴ As shown in Figure 4 (c), the relationship between
 155 the peaks intensities and the d electron number was fitted to be a linear function. The
 156 observed linear function between band intensity ratio and electron population in the
 157 TM 3d state in Figure 4 (b) provides a framework to roughly estimate the
 158 hybridization level between O 2p and metal 3d orbitals, particularly when studying
 159 interfaces of heterostructure TMOs e.g. electron enrichment at the interface between
 160 Fe_2O_3 and TiO_2 .²⁴

161 2.2.2 XES spectral features of 3d TMOs

162 Similar to resonant Raman scattering, RIXS is plotted on an energy loss scale. As
 163 indicated in Figure 3, inelastic peaks with constant energy loss follow the elastic peak

19 Figure 5: Ti L-edge RIXS spectra (bottom panel) of P25- TiO_2 and TiO_{2-n} collected with excitation
 20 energies at the Ti L-edge XAS spectra (top panel). The RIXS spectra are plotted at energy loss scale by
 subtracting the emission energy from the corresponding excitation energies.

164at 0 eV and d-d excitation, otherwise not allowed in the XAS process, is are detected
 165since the energy of the excited states is measured following resonant excitation and
 166de-excitation processes. Looking at the RIXS spectra of TiO₂ films at excitation
 167energies as indicated in Figure 5 two main features are observed: (i) an elastic peak at
 1680 eV and (ii) inelastic features at -4~15 eV. Note, the inelastic peak comprised of
 169both fluorescence signals (from Ti 3d → 2p) and Raman scattering (originating from
 170occupied O 2p orbitals to unoccupied Ti 3d orbitals).^{22, 24, 25} The appearance of the
 171energy loss features indicates the occurrence of the strong Ti 3d - O 2p hybridization.
 172For the RIXS spectra, d-d excitation feature as labeled in Figure 5 is particularly
 173interesting. The d-d excitation process, otherwise not allowed in the XAS process, is
 174detected in the excitation and de-excitation process, once the 3d orbital is partially
 175occupied. Given the 3d⁰ configuration of Ti⁴⁺ ions in the TiO₂ d-d excitation is not
 176observed, as indicating in the Figure 5. On the contrary, the d-d features at energy
 177range of -0.6 ~ -3 eV is readily observed for TiO_{2-n} sample.^{27, 28} The d-d excitation
 178features originate from two scenarios. Assuming the 3d¹ configuration for sample
 179TiO_{2-n}, the 2p core level electron can be excited to the unoccupied Ti³⁺ t_{2g} and Ti³⁺ e_g,
 180once the excitation energy tuned at energy 1 and 2 as labeled in Figure 5, respectively.
 181Following the previous 3d electron at the occupied Ti³⁺ t_{2g} will refill the 2p core
 182vacancy, leading to the formation of the d-d excitation feature. These two features are
 183named as Ti³⁺ t_{2g} resonance and Ti³⁺ e_g resonance, corresponding to the selected
 184excitation energy locating at t_{2g} and e_g XAS resonances, respectively.²⁴ The energy
 185difference of the Ti³⁺ e_g resonance d-d feature with respect to the elastic peak

186represents the magnitude of the crystal-field splitting, wherein the ground state is
187without the core hole potential effect.^{29, 30}

1883. Electronic structure of TMOs

189The overall band structure of TMOs, including the relative energy position of their
190energy band edges, local electronic structure surrounding the constituent atoms as
191well as chemical composition and morphological properties (size/shape) are crucial to
192their performance in photoelectrochemical reactions.³¹ Particularly, down scaling the
193size of e.g. nanoparticles alters the electronic properties in that the energy levels in the
194materials become much more discrete and well defined.¹⁶ Introduction of impurity
195elements into the 3d TMO' lattice may greatly alter their conduction and valence
196band, depending on the nature and concentration of the impurity elements,^{1, 32} Since
197ultimately the local interaction between impurity elements and the host matrix
198including related alteration in the local charge symmetry surrounding the host
199atoms/molecules defines the materials overall properties and performance in devices.
200It is of great interest to establish a solid correlation between *synthesis – electronic*
201*structure – device performances*.

2023.1 Studies of Pristine 3d TMOs: size effects on the TiO₂, Fe₂O₃ and ZnO

203Alteration of the electronic properties following size reduction is often referred to as
204quantum confinement effect. One striking signature of this effect is the widening of
205the bandgap.³³⁻³⁵

206The bandgap is typically categorized as (i) direct or (ii) indirect. As demonstrated in
 207Figure 6 (a), X-ray spectroscopy offers important capabilities to both project and
 208differentiate between *direct*- and *indirect* bandgaps. In the case of a direct bandgap

Figure 6: (a) Schematic representation illustrating the excitation dependence RIXS process for direct and indirect bandgap measurements. O K-edge RIXS spectra of BiVO₄ with indirect bandgap have been recorded in (b), while N K-edge RIXS spectra of InN with direct bandgap have been recorded in (c). (b) Reprinted from Ref. 36. Copyright (2007), with permission from Society of Photo Optical Instrumentation Engineers. (c) Reprinted from Ref. 41. Copyright (2015), with permission from The Royal Society of Chemistry.

209material complex, the highest onset position of the XES, i.e., the VBM, occurs at the
 210excitation energy tuned at the lowest absorption energy, i.e., the CBM. Therefore,
 211with increasing excitation energy, absorption to unoccupied states occurs well above

212the CBM, inducing the emission occurs lower than the VBM under the momentum
 213conservation rule. Thus, the highest position of the emission spectra can be obtained
 214when the excitation energy tuned at the CBM position. And as the excitation energy
 215increased, the redshift of emission spectra will be observed. This process has been
 216clearly recorded on the N K-edge RIXS spectra of IaN , showing as the redshift of the
 217emission spectra since the excitation energy increasing from 397.2 eV to 427 eV
 218(Figure 6 (b)).³⁶ On the contrary, in the case of indirect bandgap semiconductor, the
 219emission occurs at a lower lying occupied states than the VBM when the excitation
 220energy tuned at the CBM position. When the excitation energy increases, the yielded
 221emission occurs from the occupied state closer to the VBM, inducing a blue-shift of
 222the emission spectra with the increasing excitation energy starting from the CBM
 223position. Therefore, RIXS spectra with the excitation energies in the vicinity of the
 224absorption threshold are commonly monitored to judge the semiconductor bandgap
 225category. Through the RIXS investigations, the aforementioned blue-shift of the X-ray
 226emission, which corresponds to the occurrence of the indirect bandgap, has been seen
 227in diamond, Be chalcogenides, metal doped and pristine BiVO_4 , and Fe_2O_3 .³⁷⁻⁴¹
 228To further demonstrate the correlation between size and band gap we refer to previous
 229studies on the electronic properties of Fe_2O_3 by Vayssieres et al.^{40, 42} Previously,
 230Gilbert and Vayssieres et al. have investigated the size dependent electronic structures
 231evolutions of hematite. Gilbert et al. have monitored the bandgap by using the O K-
 232edge XAS/XES.⁴⁰ By tuning the excitation energies across the XAS onset through the
 233 e_g feature position to above the non-resonant post-edge, a new state was clearly

234observed at the high emission energy region. The blue-shift of the emission spectra is
 235a strong indication that Fe_2O_3 is an indirect bandgap semiconductor.⁴⁰ Therefore, the
 236bandgap has been determined by measuring the energy differences between the
 237inflection points near the CBM of the O K-edge XAS and VBM of the O K-edge nr-
 238XES, respectively. As a consequence, the obtained bulk hematite bandgap value
 239showed great consistence with the value obtained from the optical spectroscopy.
 240Following, the size effects in the electronic structure of Fe_2O_3 have been investigated
 241by monitoring the bulk and nanoscale hematite NPs with three different sizes, namely
 242the bulk materials, 30 nm and 8 nm NPs. By employing the O K-edge XAS/nr-XES
 243spectra of these three samples, no detectable shifts have been noted. It indicated that
 244the bandgap values of hematite samples with particle size down to 8 nm were
 245identical. However, it has also been demonstrated that significant quantum
 246confinement effect occurred on the hematite ultrafine nanorod arrays.⁴² Vayssieres et
 247al. have monitored the bandgap by using the Fe L-edge XES, including the nr-XES
 248and RIXS. For the Fe L-edge nr-XES, two broad features L_α and L_β are observed,
 249which originate from the transition from the $2p_{1/2}$ and $2p_{3/2}$ to the 3d orbital,
 250respectively.⁴³ The branching ratio of the L_β/L_α is directly influenced by non-radiative
 251Coster-Kronig transition between L_2 and L_3 in the absorption process, which is
 252determined by the bandgap value.⁴⁴ It has been well established that the higher
 253bandgap value gives rise to the higher intensity ratio of the $I(L_\beta)/I(L_\alpha)$. Besides the
 254judgment driving from the nr-XES, RIXS can also be employed to determine the
 255bandgap value. The $3d^5$ configuration of the Fe cations in hematite induces the

256 appearance of several well identified d-d excitation and charge transfer features,
257 which locate at 1.0, 2.5, 3.3 and 5.6 eV below the excitation energy.^{42, 45} The 1 eV
258 energy-loss feature originates from the multiple excitation transition; the 3.3 and 5.6
259 eV features correspond to the charge transfer between the O 2p and Fe 3d bands; and
260 the 2.5 eV feature reflects the bandgap transition. It was found that the $I(L_\beta)/I(L_\alpha)$
261 ratio increased and the bandgap transition feature blue shifted when the nanorod
262 diameter tuning from bulk down to 4-5 nm. The findings indicated that the quantum
263 confinement effect occurred on the hematite nanorods. The widening of the ultrafine
264 hematite nanorods bandgap suggested that it is possible for the water photo-oxidation
265 happens without external applied bias with well-designed material.

266 To further elucidate the quantum confinement effect on the TMOs. TiO_2 NPs with
267 different sizes have been investigated by experiment and theoretical simulation. The
268 decrease of the NPs size induced the increment of the surface to volume ratio, which
269 reflects the higher portion of the surface atoms in the NPs. Due to its core-like nature,
270 the Ti 3d orbital becomes less dominating in comparison with the Ti 4s4p orbitals by
271 decreasing the TiO_2 particle size.⁴⁶ The orbital ratio change can significantly alter the
272 spectra profiles of the O K-edge XAS through hybridization between the Ti orbitals
273 and O orbitals. O K-edge XAS of TiO_2 NPs with sizes of 200, 20 and 2 nm are
274 recorded in Figure 7 (a). By reducing the particle sizes, two spectra profiles changes
275 can be observed: (i) the broadening of absorption features and (ii) the decreasing of
276 the peaks intensities below the ionization threshold. They can be ascribed to the loss
277 of the crystalline structures and the appearance of strong covalency at small particle

size. The local average arrangements on the Ti sites induced the broadening of the absorption features when the TiO₂ structures showed a loss of the long-range order at a length scale of around 1 nm.^{23, 47} Moreover, the covalency reduced the occupation level of the original fully filled 2p states, thereby influencing the strength of the hybridization between O 2p and Ti 3d. Strong covalency of the NPs and decreased Ti 3d orbital portion induced the decreasing of the O 2p-Ti 3d features at reduced particle size. in the computed spectra in Figure 7 (b) demonstrate a red shift with decreasing particle size that reduces VBM-CBM energy separation. Furthermore, observing from the XAS spectra profiles and combining with the aforementioned 3d-sp band intensity ratio evolutions²⁴, it can be inferred that the number of unoccupied d states available for mixing with O 2p states decreased at the 2 nm TiO₂ NPs with respect to that at the 200nm TiO₂. This shows great accordance with the size dependent Ti 3d/4sp band distribution.

As discussed above, the size effect in 3d TMOs can be derived from the surface

Figure 7: (a) The O K-edge XAS of TiO₂ NPs with particle sizes of 2 nm, 20 nm and 200 nm, (b) the simulation results of the O K-edge XAS of nano and bulk TiO₂ NPs, the atomic resolved density of state of s- and p-like states were shown in the inset, (c) O K-edge XAS of ZnO quantum dots with particle sizes of 6, 12, 20 nm, the O K-edge spectra after background subtraction were shown in the inset. (a)(b) Reprinted from Ref. 46. Copyright (2011), with permission from AIP publishing. (c) Reprinted from Ref. 48. Copyright (2007), with permission from AIP publishing.

292curvature, which showed great relevance with the radial distribution of the 3d/4sp
 293bands. One should be noted that this effect may not be the prominent reason for the
 294spectra profiles changes of all the 3d TMOs. In the case of ZnO, Zn cation showed
 2953d¹⁰ configuration, where no unoccupied d band sites are available for mixing with O
 2962p. The particle size induced change of radial distribution of 3d/4sp bands is missing.
 297Ray et al. has investigated the O K-edge XAS of ZnO quantum dots (QDs) with
 298particle sizes from 20 nm down to 6 nm.⁴⁸ The features B₃ at the energy region of 530-
 299545 eV showed a significant decrease, as shown in Figure 7 (c). Considering the
 300signature quantum confinement effect induced optical properties were absent in the
 301ZnO QDs and the particle size is higher than the exciton Bohr radius (1–2 nm), the
 302quantum confinement effect was considered not to be responsible for the electronic
 303structure changes. With angle-dependence XAS studies, it has been well documented
 304that the feature B₃ originated from the O 1s to O 2p π orbital transition, which lies
 305along the c axis of the QDs.^{49, 50} The decrease of the particle size made the particle
 306much closer to the sphere and no favorable orbital orientation existed. As a
 307consequence, the poor alignment between the O 2p π orbital and electric field was
 308obtained, inducing the lower intensity of peaks B₃. With the increase of the particle
 309size, the orientation became ordered and good alignment between O 2p π orbitals and
 310electric field was achieved, thereby stronger intensity of peak B₃ was observed.
 311Through these investigations, the size dependent electronic structures on both cations
 312and anions of various 3d TMOs have been well resolved by employing the soft X-ray
 313spectroscopies. The unique advantages of soft X-ray spectroscopies have been well

314exhibited in these systems, due to the fact that the changes on the morphology
315(size/shape) directly tailored the materials properties by altering the electronic
316structures of the materials.

3173.2 Properties of doped 3d TMOs, examples of TiO_2

318In addition to chemical composition, many materials properties (e.g. electronic,
319optical, magnetic etc.) can be altered by controlling the lattice defects (e.g. *oxygen*
320*vacancies*, *cation vacancies*, *cation* and *oxygen interstitials*.) therein, both at the
321surface and in bulk..^{1, 32, 51-58} Specifically, extraction/insertion of O atoms from/to
322stoichiometric materials may induces the reduction/oxidization properties as it
323disturbs the local charge symmetry surrounding the constituent atoms across the
324lattice, example includes: TiO_{2-x} , $\text{Ti}_{1+x}\text{O}_2$ and TiO_{2+x} , $\text{Ti}_{1-x}\text{O}_2$, respectively. Normally,
325these scenarios can be ascribed to the change of the oxygen environment. Few studies
326relevant to the oxygen interstitials are available up to date. It has shown that, oxygen
327rich is realized by forming a bridge oxygen bonding (-O-O- bond) instead of being
328stabilized in the crystal structure interstice.³² The formation of the -O-O- bond
329required special treatment. Commonly, it was investigated in a model system and was
330constructed and studied on single crystal samples, while the scanning tunneling
331microscope was always employed to monitor relevant properties.^{59, 60} Moreover, the
332theoretical simulations indicated that this kind of bond can be good electron trap,
333where the extra electrons from the O can occupy the σ^* states. Consequently, the
334drastic change on the band structures can be predicted. Therefore, it can be expected
335that XAS/XES can provide further insight on this bond and its relevant properties,

336which is in a big lack up to now.
 337Oxygen vacancies, i.e. removal of a neutral oxygen atom, is readily induced by
 338thermal annealing, UV illumination and/or doping.^{61, 62} It is generally recognized that
 339formation of Ti^{3+} is favored with the creation of the various deficiencies at anion
 340lattice sites,^{1, 32, 63} particularly existence of Ti^{3+} species following O vacancies has been
 341widely studied.^{64, 65} Removal of an oxygen atom leaves two excess electrons at the
 342vacancy site. Surrounding Ti sites include the original six fold Ti^{4+} and **under-**
 343**coordinated** Ti^{3+} . Each **under-coordinated** Ti^{3+} traps an excess electron while second
 344electron remains delocalized.⁶⁶ Reflecting back on the correlation between lattice
 345defects and relative energy separation between CBM-VBM, oxygen vacancies in TiO_2
 346can produce a delocalized donor state near the bottom of the conduction band, or a
 347state within the bandgap, 1 eV below the CBM.^{32, 67}
 348However, it should be noted that, the true origin of partially reduced TiO_2 i.e. anion
 349deficiency or excess of cations is still under debate.³² Theoretical studies have
 350indicated that (in most cases) the Ti interstitial model can be utilized in a way
 351analogous to the of O vacancies model. Clearly, defect structure, i.e. nature and
 352concentration of defects, strongly correlates to the electronic properties in
 353semiconductors and play an important role towards improving and optimizing their
 354overall functional properties.

355As previously mentioned, there are various routes to induce oxygen vacancies.
 356Among these, doping is still the most commonly employed method by which metal
 357ions of lower valence state than parent 3d TM cations are introduced into the TMO

Figure 8: The O K-edge XAS of P25-TiO₂ and TiO₂ doped with Ba. The O2p-Ti3d hybridization peak splits to t_{2g} and e_g sub-peaks due to the crystal-field strength.

host lattice..⁶⁸ Similarly, cation vacancies also induce partially occupied orbitals within the bandgap which is typically manifested as change in the relative intensity of t_{2g}/e_g spectral features. Also, the peak intensities decrease and changes of the t_{2g}/e_g peak intensity are easily detectable within systems.^{69, 70} However, one should be aware of the solubility of impurity elements, before they agglomerate and result in phase separation, which is typically less than 5% for TMOs, depending on crystal structure. While this may seem low, it has been reported that even at doping concentrations as low as 0.1% (equal to 5×10^{19} donors/cm³) may induce donor level within the bandgap near the CBM.⁶⁸ Going back to TiO₂, since formation of oxygen vacancy is always associated with the presence of Ti³⁺ Ti L-edge RIXS d-d spectral feature is a fingerprint on occurrence of oxygen related lattice defects. Moreover, since the oxygen vacancy induced donor state overlaps with the CBM it decreases the probability of core level $\rightarrow$ conduction band transitions and clearly evident in the absorption spectra. As a result, the relative intensity of the O K-edge XAS pre-edge features decreases. This has clearly been exemplified by Yan et al. in Ref. 67 and Wang et al. in Ref. 68 wherein the authors have reported on the evolution in the TiO₂ XAS upon doping with Co and Ba, respectively.^{67, 68} As shown in Figure 8, the O K-edge XAS spectra showed dramatic changes with the introduction of the Ba to the TiO₂ lattice. The decrease of the t_{2g} peak is a strong evidence for the formation of the oxygen vacancy. Also, the broad post-edge features can be attributed to the distortion of the crystal structure, which implies that the dopant also induced the change of the lattice structures.

380 Different from metal doping, non-metal doping influences the valence band via
381 electronic transitions between the impurity 2p (N, F and C) and 3p (S) orbitals, and
382 the Ti 3d orbital.⁷¹ Nitrogen doped TiO₂ is a good example of non-metal doping
383 induced localized states near the valence band region within the band gap. Further, the
384 change of the anion sites altered the short-range and medium-range cation
385 environments concomitant with the crystal structure change.⁷² As a consequence, on
386 the N-doped TiO₂, it has been noted that (i) the intensity of antibonding O2p
387 absorption feature increased in the O K-edge XAS and (ii) the changes of the crystal
388 structure favored the rearrangement of the e_g orbitals, representing with an additional
389 e_g state peak formed between the t_{2g} and e_g peaks.⁷² Furthermore, due to the localized
390 state in the bandgap, the energy barrier of the formation of an oxygen vacancy was
391 substantial reducing, favoring the creation of the oxygen vacancies at the high N
392 doping level.³² With quantitative analysis on the O K-edge XAS of N-doped TiO₂ and
393 the catalytic performance, the structure-performance correlation is obtained.

Besides, Chuang et. al, has observed the electronic structures evolutions of N doped TiO_2 nanocrystals (NCs) by employing the Ti L-edge XAS and RIXS. Herein shows

Figure 9: (a) Ti 2p absorption spectrum of TiO_2 , N: TiO_2 NCs, and standard $\text{TiO}_2/\text{Ti}_2\text{O}_3$ samples, by means of total electron yield mode. (b) Ti L-edge RIXS spectra measured at the different incident energies.

the electronic structure environment of nitrogen-doped TiO_2 (NTO) and pristine TiO_2 NCs by both the nanoscale and nitrogen doping influences, shown in Figure 9(a)(b). The absorption peaks of TiO_2 NCs are very similar to that of NTO NCs, and there are characterized as the anatase phase by the comparison of standard TiO_2 . The main spectral performance is recognized as Ti 2p to 3d transition, separated by $2p_{1/2}$ and $2p_{3/2}$ levels due to the spin-orbit coupling. Besides, the fine structure for t_{2g} and e_g states is derived from the crystal field splitting of Ti 3d state, where its split structure can be indicative of the specific lattice and electronic environment. On the other hand, one 3d electron ($3d^1$ configuration) in the standard Ti_2O_3 exhibits the slightly energy-forward shift of peaks and wide spectral width in the absorption spectra, different from empty 3d electron in TiO_2 . Figure (b) shows the Ti *L*-edge resonant emission spectra of TiO_2 and NTO NCs, to signify the variation of charge transfer and d-d excitation under the nanoscale dimension. The excitation energy selected to the Ti 2p-3d absorption region certifies the origin of Raman and fluorescence components different. The spectra as a function of the energy loss (from the excitation energy) exhibit two Raman peaks ($0 \sim 4.0$ eV) and one broad fluorescence structure ($4.0 \sim 12.0$ eV), while the incident X-ray energy is fixed at the excitation energy by $h\nu = 457.2$ and 458.6 eV (black bars in (a)). The Raman peak at 1.3 eV in the lower excitation energy (457.2 eV) is shifted to higher energy-loss position at 2.6 eV as probed at the higher excitation energy (458.6 eV), attributed to the delocalized d-d electron interaction. The peak at 2.6 eV and new raising peak at 1.2 eV are assigned to the electron coupling between t_{2g} - e_g and t_{2g} - t_{2g} sublevels individually.³⁰ The

involvement of nitrogen doping contribution lowers the signal of Raman peaks by the co-existed bonding environment between anion oxygen and nitrogen site. The band in the energy-loss range of 4.0 and 12.0 eV is assigned to the charge transfer hybridization, depending on the excitation energy selection. The detailed band-structure mapping of TiO₂ NCs is shown in the previous literature. Its nitrogen doping into the pristine TiO₂ NCs causes the band narrowing near the bottom level of valence band. In short, while the nanoscale fabrication is applied to reduce the bulk TiO₂ materials, the lattice vacancy formation on the NCs surface results in the Ti³⁺(3d¹) transition and the following inter/intra d-d interaction. Taking into account the doping N atom, the hybridization between cation Ti and ligand O site give the insensitive change in the unoccupied state, but the unique Ti³⁺(3d¹) configuration offers the strong electron correlation to vary the valence band and d-d coupling during the absorption/de-excitation process.

While computational studies on the role of oxygen vacancies on the electronic properties of 3d TMOs has reached a state of maturity systematic experimental practices on the same is lacking and needs to be addressed in order to bring further advances in materials development.

4. Recent progress on *in-situ/operando* X-ray spectroscopy techniques

While X-ray spectroscopy (predominantly ex-situ) has been widely employed to study materials properties in various capacities to gain deep insight on important materials properties, very few have taken a step further to investigate the same under nearly identical to operational conditions. Along this line, Braun et al. have contributed

significantly on the pioneering of *in-situ/operando* X-ray spectroscopy studies.^{73, 74}

At first, hematite films on FTO were treated under solar illumination with external electrochemical potential. It has shown that significant changes on the O K-edge XAS profiles occurred on the post-treated sample, including the changes of peaks intensities and the appearance of a new feature between the O2p-Fe3d and O2p-Fe4sp features.⁷⁴ The newly formed feature has been confirmed to be relative to a state near the VBM, origination from the transition from O 1s to the upper Hubbard band with a strong Fe 3d character. This observation suggested that the electronic structures of hematite changed during the electrochemical oxidation process. With further studies, it has found that the spectral profiles resembled those of the Si-doped hematite well, providing further support for the origination of the potential induced electronic structure changes. Inspired and promoted by this work, Braun et al, utilized an *in-situ/operando* design to achieve the direct observation of the electronic structures of an operating 1% Si-doped hematite photoanode that was used to catalyze photoelectrochemical water splitting.^{73, 75} It has shown that, O K-edge XAS of the photoanode did not show significant change with external potential applied in the dark condition. On the contrary, two new features formed when the external potential applied between 300 to 700 meV with solar light illumination. The two newly formed features are ascribed to an O 2p type hole transition into the charge transfer band and the strong Fe 3d type hole transition into the upper Hubbard band, respectively, from low to high-energy region. This is the first time to carry out the direct *in-situ/operando* analysis of the electronic structure of a photoanode. A large portion of

the reason of the successful operated experiment should be ascribed to the well-performed *in-situ/operando* electrochemical cells. The schematic of the experimental device has been displayed in Figure 10 (a) and (b).

Soft X-ray region, such as O K-edge and TM L-edge, measurements require vacuum chambers because of the strong interactions between photons and gas molecules under ambient pressures. The vacuum requirement makes it challenging to carry out direct

Figure 10: (a), (b) The Schematic of cell assembly and mapping of the *in-situ/operando* X-ray cell; (c) the model of a newly developed cell, the sunlight and X-ray beams go through the electrolyte layer and the electrode/electrolyte interface can be observed; (d) a X-ray modulate device that can separate the electrochemical current and X-ray beam induced current, which can provide clean TEY signal at the electrode/electrolyte interface. (a) Reprinted from Ref. 73. Copyright (2012), with permission from American Chemical Society. (b)(d) Reprinted from Ref. 77. Copyright (2015), with permission from The Royal Society of Chemistry.

468 measurements on liquid and/or solid layers using conventional experimental setups.
469 One strategy to overcome the pressure gap between the measurement system and the
470 reaction system is to use X-ray transparent membrane to encapsulate liquid containing
471 reaction system. With substantial efforts in instrument development, such
472 encapsulation or liquid cell strategy has been proved to work well. (Ref, JESR
473 review) Common materials for such X-ray transparent membranes include Si_3N_4 ,
474 SiO_2 , Si and graphene. Of them, Si_3N_4 window is the most commonly employed
475 materials to separate the cell chamber from the UHV system. The Si_3N_4 window
476 (typically 100 nm) can tolerate up to 1 MPa pressure difference, while ensuring the
477 sufficient X-ray transition. The liquid layer (electrolyte) was incorporated in the cell
478 by the Si_3N_4 window, and the liquid inlet and outlet allowed refreshing electrolytes
479 during the experiments. The Si_3N_4 window was coated with Cr and Au to improve the
480 conductivity and the adhesive to stabilize the hematite anode. This multilayer film
481 acted as the working electrode, while the Pt wire and Ag/AgCl were employed as
482 counter and reference electrodes, respectively. The three-electrode configuration made
483 it possible to run electrochemistry inside the cell and perform *in-situ/operando* sXAS
484 measurements. During the electrochemical process, the hematite film was controlled
485 to be either in dark or under illuminated with a solar simulator, the light of which was
486 directed through the Si_3N_4 window. This specially designed device facilitated the *in-*
487 *situ/operando* studies of catalyst that can be utilized in photochemical and
488 electrochemical reactions.

489 Classic electrochemistry theories, mostly continuum theories, suggested that

490electrode/electrolyte interface plays a vital role in various electrochemical systems. It
491is crucially important to understand the interfacial properties involved in relevant
492electrochemical reactions to achieve optimum performance of the electrochemical
493devices. Therefore, the capability to directly and accurately characterize the properties
494of the interfaces is extremely important to the energy community. In most work, since
495the mean free path of electron is generally low (a few nanometers), the emitted
496electrons cannot pass through the Si_3N_4 window, only FY signal can be recorded to
497characterize the bulk liquid and/or solid layers. Consequently, the obtained XAS
498information is dominated by the buried sub-layer of films, while the
499electrode/electrolyte interface signals are not prominent, due to the large detection
500depth of fluorescence signal. Thereby, some new cell designs have been proposed,
501which may be helpful to get more accurate information relevant to the
502electrode/electrolyte interface, as shown in Figure 10 (c). A small modification is
503applied on the previous cell configuration. In this design, the thickness of the
504electrolyte has been controlled to be a thin layer. By reducing the thickness of the
505liquid layer and replacing the counter cell body with a Si_3N_4 window, it is able to
506directly monitor the front side of the materials of interest, which is the surface
507immediately attached to the electrolyte. Considering the attenuation of X-rays through
508the electrolyte, the detection depth is highly reduced, wherein more surface relevant
509information can be provided in comparison with that detected from the backside. One
510obvious shortage of this experimental setup is that this design only allows for probing
511the changes on the catalyst cation site, due to the interruption of the electrolyte signal

512with strong Oxygen contribution. Considering the strong hybridization between the O
513and cations in 3d TMOs, the information obtained from this design is still valuable for
514the better interpretation of the electrode/electrolyte interface under operation.
515As discussed in the previous sections, the TEY detection mode, which originates from
516the measurement of the secondary electron cascade, offers more surface sensitive
517information compared to the TFY detection mode. This has fueled up the scientists to
518monitor the interfacial properties under TEY detection mode. With proper
519modifications on the cell configuration shown in the Figure 10 (b), the TEY signal can
520be recorded under open circle potential state by monitoring the secondary electrode
521cascade through the working electrode. However, this approach meets a big technical
522challenges under reaction conditions with external voltage, ascribing to the interrupt
523of the electrochemical potential induced ionic current. The reaction related ionic
524current is several orders of magnitude higher compared to the photon-induced current.
525As a result, the TEY measurements were hindered under the operando condition. With
526substantial efforts devoted to the instrument development, a vacuum-capable liquid
527cell and an X-ray modulation system were developed. By applying this system, the
528dominant ionic current can be separated from the tiny TEY current via a frequency
529modulation method under electrochemical conditions. Specifically, this system
530contains a three-electrode vacuum based liquid cell, a high frequency chopper and a
531lock-in amplifier, as shown in Figure 10 (d).^{76, 77} A piezo-actuated chopper was
532introduced to modulate the incoming X-ray beam at a designed frequency.
533Intermittent X-ray generates an AC component in the overall current (including both
534ionic and TEY current), which can then be filtered out using lock-in amplifiers and

535 other necessary electronics. The new development of *in-situ/operando* interface-
536 sensitive sXAS provides new opportunities to investigate various solid/liquid
537 interfaces in various important electrochemical systems. Combining this state-of-the-
538 art X-ray modulation device setup and the *in-situ/operando* cell design showing in
539 Figure 10 (c), the electrode/electrolyte surface and buried subsurface can be
540 simultaneously detect by TEY and TFY, respectively, providing better understanding
541 on the properties of the 3d TMOs under operating condition.
542 These three different vacuum-capable cells combining with the *in-situ/operando*
543 sXAS method enable the studies of different aspects of the electrode/electrolyte
544 interface under reaction conditions, for instance the adsorption and deposition of
545 solute species on electrode surface in Mg-ion batteries, morphological and chemical
546 changes of graphene-based electrode under the influence of electrolytes and
547 potentials, and potential-dependent orientations of interfacial solvent molecules at
548 Au/water interface, just to name a few. These examples have demonstrated the
549 capability of *in-situ/operando* sXAS techniques in the investigation of different
550 aspects of the solid/liquid interfaces. Considering the interference of the oxygen
551 signals in the electrolyte, the observations on the oxygen signal can only be achieved
552 from the backside, where bulk-sensitive signals are recorded. Therefore, the
553 interfacial studies on the cation sites (TMs) can be a valuable supplementary
554 information for the studies of 3d TMOs properties during a photoelectrochemical
555 reaction. We hope that the *in-situ/operando* characterization basin on the cell
556 configurations shown in Figure 10 (c) and (d) can provide exciting new opportunities
557 for the scientists to take a closer look at the electrode/electrolyte interfaces and open

the way to the investigation of various solid/liquid interfaces in the important heterogeneous reactions evolved in the photoelectrocatalysts field.

5. Conclusion and outlook

The cases showcased in this perspective include investigation of self-constructed and doped 3d TMOs, and introductions of *in-situ/operando* X-ray cell designs that the unique advantages of synchrotron based X-ray spectroscopy. Self-construction of 3d TMOs are mainly realized by controlling morphological properties. Introducing impurities to the 3d TMOs significantly influence the band structure as localized impurity states are formed closely above or below the VBM and CBM, respectively. *In-situ/operando* characterization combines unique capabilities to emanate fingerprints on the electronic structure (on surface, at interfaces and in bulk), band gap, and band levels in real-time under conditions nearly identical to operational mode. This together with the ability to tailor the intrinsic properties of functional semiconductors at reduced scale and manipulate the morphological properties not only holds great promise for advancement in the field of renewable energy but also offers great insight into the fundamental materials properties. Owing to the spatial confined, we focused on the application of TMOs on the field of photocatalysis, it should be noted that 3d TMOs based materials can also be employed in other renewable energy technical applications including Li-ion cells, non-photoelectrocatalysis and thermoelectric materials. We hope this perspective can also open the way to the investigations of various systems relating to these techniques.

Finally, it should be mentioned that, even if the application of photoelectron

spectroscopy (PES) to the 3d TMOs studies is highly limited and interrupted by the capping agent and surface residential, the information driving from the PES are still valuable. The PES provides the information of the energy difference from the core level to the Fermi level, making it a strong support to the XAS/XES information for better interpretation of the electronic structures near the Fermi level. One way to circumvent the detection depth issue is to increase the X-rays source to higher photon energies, such as pushing to 2000 eV or above. Also, if tender X-rays are utilized as excitation source, some photochemical and electrochemical systems can be combined to provide *in-situ/operando* investigations, which is beyond our topic in this perspective and have been detailed in other works.^{75, 77}

One important point that needs to be addressed is the consequence of exposing a specimen to a highly energetic probe. Continuous illumination with high flux X-rays and the subsequently X-ray induced emitting electrons may not only deteriorate sensitive samples (e.g. biological samples) but also lead to unintentional electron doping which will falsify information of the electronic structure. Thus, it is important to take appropriate precautions to reduce the negative impact of X-ray radiation e.g. reducing the X-ray flux, defocusing X-ray beams to low the photon density, and applying cooling to the samples.

We hope all these information can provide better insight into the 3d TMOs materials synthesis and characterizations and finally achieve the further improvements of relevant to energy application.

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