Light-induced breathing in photochromic yttrium oxyhydrides

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The origin of the photochromic mechanism in YHO is still open to debate and has been attributed to different causes [13–15]. In the present paper, the study of the wettability of the YHO surface under illumination and darkness conditions, as well as the photochromic darkening/bleaching dynamics in air and in inert atmosphere, unraveled the cause that underpins the photochromism in YHO.

According to our observations, oxygen diffusion takes place during illumination (consequently, the YHO lattice contracts). The displaced oxygen atoms leave behind an oxygen-deficient structure responsible for the optical darkening, which is in agreement with our previous observations [13]. In darkness, the YHO lattice expands back as a consequence of the filling of the oxygen vacancies by oxygen atoms, allowing the film to bleach back to its original state. Since YHO expands/contracts reversibly under dark/illumination cycling produced by the displacement inwards/outwards of oxygen atoms, we refer to this process as breathing.

Due to this breathing, the correct bleaching of the photodarkened YHO coatings depends on the availability of an oxygen source. Thanks to the light-induced oxygen diffusion, YHO could be used for other purposes such as sensing and optical memories, broadening the traditional fields of application of photochromic materials.

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The wettability of YHO under illumination is unusual. All oxides and nitrides of low-electronegativity metals can exhibit hydrophobicity [16,17]. Therefore it can be expected that YHO exhibits hydrophobic properties as well. However, while the surface of yttrium oxyhydride increases its hydrophobicity when illuminated, other metal oxides become hydrophilic under UV illumination. In the latter case, the formation of electron-hole pairs under illumination leads to the creation of defect sites where hydroxyl groups can be adsorbed, leading to hydrophilic properties [18]. Generally, when metal oxides are stored in darkness during periods of time ranging from 7 to 50 days [19,20], oxygen replaces back the adsorbed hydroxyl groups, giving raise to hydrophobicity. In the present work, the unexpected behavior observed in YHO, i.e., the enhancement of the hydrophobic properties under illumination, has been found to be caused by the same reason, that is, the oxygen enrichment of the surface under illumination.

II. METHODS

YHO thin films were prepared onto glass substrates following a two-step deposition process. First YH₂ metallic films were fabricated by magnetron sputtering in a Leybold Optics A550V7 sputter unit. Second, postdeposition oxidation in air transformed YH₂ to YHO. In order to achieve YHO upon air exposure, precursor YH₂ films have to be deposited when the chamber pressure is above a certain critical value, which results in films with large structural disorder [21]. Further details on the synthesis process of photochromic YHO, both intrinsic and doped with Zr, can be found elsewhere [3,21,22]. A cold white LED array from Thorlabs (color temperature 4600–9000 K) was used as an illumination source for the photodarkening experiments. The crystallographic structure of the obtained films was characterized by using x-ray diffraction (XRD) in a Bruker Siemens D500E spectrophotometer (Cu Kα radiation, parallel beam geometry). The composition and surface oxidation states were studied by x-ray photoelectron spectroscopy (XPS) in an Ulvac PHI Quantera II instrument. Surface roughness characterizations were performed using atomic force microscopy with area of 5 µm² from a PhotonIc Technologies picostation. The optical transmittance (T) of the YHO films in the clear and photodarkened state was measured using an Ocean Optics QE65000 spectrophotometer and a Perkin-Elmer Lambda 900 with an integrating sphere. Contact angle (CA) measurements were performed using a KSV Attension optical tensiometer under air. A 5-µl drop volume was used for each CA measurement, and three different sessile droplets were measured on several substrates for each value and averaged with a standard deviation of ±2. CA values in the equilibrium (θₑ) for water, ethylene glycol (EG), and methylene iodide (MeI)—both EG and MeI from Sigma-Aldrich—were used to calculate surface free energies of yttrium oxyhydride films at clear and photodarkened state using the van Oss–Good–Chaudhury method [23,24].

The calculations were performed with the Vienna Ab Initio Simulation Package (VASP) code [25–27], based on density functional theory (DFT), using a plane-wave pseudopotential method together with the potential projector augmented wave (PAW) [28–30]. The generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof (PBE) is used to describe the exchange-correlation functional [27]. To describe the electron-ion interaction standard PAW-PBE pseudopotentials [31] are used with 1s¹ for H, 2s²2p¹ for O, and 4s²4p⁰4d¹5s² for Y atoms as the valence-electron configuration. The plane-wave functions of valence electrons are expanded in a plane-wave basis set, and the use of PAW pseudopotentials allows a plane-wave energy cutoff ($E_{cut}$). Only plane waves with kinetic energies smaller than $E_{cut}$ are used in the expansion. Reciprocal-space integration over the Brillouin zone is approximated through a careful sampling at finite number of k points using a Monkhorst-Pack mesh [30]. We choose the energy cutoff to be 700 eV, and the Brillouin-zone sampling mesh parameters for the k-points set are 8 × 8 × 8. In the optimization process the energy change is set to 1 × 10⁻⁶ eV. The charge densities are converged to 1 × 10⁻⁶ eV in the self-consistent calculation. The range-separated hybrid Heyd-Scuseria-Ernzerhof (HSE06) functional is used for density-of-states calculations [32–34]. The hybrid functional requires a standard value of the (short-range) Hartree-Fock exchange (21%) mixed with a portion of PBE exchange (79%), also known as the HSE06 hybrid functional [33,34]. Selection of the parameter has been performed as an inverse value of infinity dielectric constant that is valid, if the energy band gap of these systems is larger than 3 eV.

III. RESULTS AND DISCUSSION

A. Hydrophobicity control through light illumination

YHO thin films exhibit photochromic properties, that is, YHO films undergo a reversible decrease of their optical transmittance when illuminated with light of adequate energy and intensity [22]. Figure 1(a) shows the transmittance in the visible region of 500–700 nm for a 1400-nm-thick YHO film. This film decreased its luminous transmittance $T_{lum}$ [35] from 78.5% to 26.7% after illumination. The luminous efficiency of the human eye (photopic vision) is presented in Fig. 1(a) for comparison. How to obtain such optical contrast by illumination will be discussed in detail in the next section. Recent studies by Nafezarefi et al. [21] revealed that the bleaching dynamics and photochromic contrast in YHO is affected by Zr doping.

Nonilluminated (clear) YHO thin films show hydrophobicity with equilibrium contact angle $θ_e$ values of 95° for water (see Table I); however, $θ_e$ values increased to 115° after illumination (again in the case of water), see Table I and Fig. 1(b). Table I also shows $θ_e$ for ethylene glycol EG and methylene iodide MeI for the clear and photodarkened states. In the case of MeI, $θ_e$ also increases after illumination, from 43° to 60°, yet remains constant for EG. Atomic force microscopy AFM studies performed in such films revealed a relatively smooth surface with a rms value of surface roughness of around 8 nm.

The observed initial hydrophobicity of the YHO films (clear state) can be explained by the electronic structure of rare-earth elements. According to a detailed experimental analysis of the entire rare-earth oxide series carried out by Azimi et al. [17], the unfilled 4f orbitals shielded by a full octet
of electrons from the 5s2p6 shell result in a lower tendency of such compounds to form hydrogen bonds with the adjacent water molecules [17,36]. Hydrophobicity is not exclusive of the lanthanide f-shell group, but it can be achievable in any metal oxide provided that the electronegativity of such metal is low enough [16]. The low electronegativity of Y and the prevalence of yttrium oxide at the surface [37] explains the high θe shown in Table I.

One might expect decreased hydrophobicity under illumination caused by electron-hole pairs. Such behavior occurs in other metal oxides [18,19,38–41]. As we stated previously, however, hydrophobicity in YHO is enhanced under illumination. The light-induced decrease of wettability can be explained through changes in the oxygen-to-metal ratio at the surface. In metal oxides, coordinatively unsaturated oxygen atoms work as a Lewis base while the metal cations work as surface. In metal oxides, coordinatively unsaturated oxygen atoms can result in a lower tendency of such compounds to form hydrogen bonds with the adjacent water molecules [48]. In particular, the decrease in carbon content can result in an increase of the intensity of the O1s contributions located at higher energies [44]. Nevertheless, a decrease in carbon content can result in an increase of the intensity of the XPS contributions located at higher energies [48]. In particular, the decrease of carbon may result in an increase of the O1s intensity when compared to the intensity of the Y3d signal. For this reason, O/Y ratios in Table II have been calculated using Y3s and Y3p levels, which are closer in energy to O1s than Y3d.

The O1s signal is composed of two contributions at 529.0 and 531.2 eV. The former can be attributed to O atoms bound to Y atoms, whereas the latter can be assigned to atomic oxygen [49]. After illumination, the oxygen-to-yttrium atomic ratio of the surface increases, see Table II. This increase is consistent when comparing the O1s level to Y3s and Y3p levels, and takes place both for O bound to Y as well as for atomic O. The largest increase is observed in the latter.

The carbon (adventitious) C1s signal can be deconvoluted into three different contributions. The signal corresponding to C-C has been established at 284.8 eV as a charge correction reference. Other contributions are located at 286.3 eV (attributed to C-O-C and/or C-OH, which are expected to present a ~0.1-eV difference in energy and hence are difficult to resolve), and O-C = O at 288.8 eV [44].

After illumination, the carbon content on the surface decreases, see Table II. This decrease is more pronounced in the C-C contribution, Fig. 1(c). Since the content of C in the surface decreases, the increase of adsorbed hydrocarbons is ruled out as the possible cause for the light-induced enhancement of the hydrophobicity [45–47]. Nevertheless, a decrease in carbon content can result in an increase of the intensity of the XPS contributions located at higher energies [48].

In order to study the compositional changes of the YHO surface, XPS measurements were performed before and after illumination. The results are presented for C1s, O1s, and Y3d in Fig. 1(c). See Table II for the quantification of the different elements by XPS. The quantification has been done using survey spectra (not shown) considering Y3s, O1s, and C1s (column A) or Y3p, O1s, and C1s (column B) for both the clear and dark state.

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### Table I. Equilibrium contact angle values (θe) for water, ethylene glycol (EG), and methylene iodine (MeI), as well as the measured total surface energy (γtotal) and its components: Lifshitz–van der Waals interactions term (γLW) and acid-base interaction term (γAB)—calculated from the Lewis acid and base parameters (γ+ and γ−, respectively). All data given for the clear and photodarkened state.

<table>
<thead>
<tr>
<th>State</th>
<th>θe (Water) (deg)</th>
<th>θe (EG) (deg)</th>
<th>θe (Mel) (deg)</th>
<th>γLW (mJ/m²)</th>
<th>γAB (mJ/m²)</th>
<th>γtotal (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clear state</td>
<td>95</td>
<td>81</td>
<td>43</td>
<td>46.55</td>
<td>8.98</td>
<td>55.51</td>
</tr>
<tr>
<td>Photodarkened state</td>
<td>115</td>
<td>81</td>
<td>60</td>
<td>28.88</td>
<td>0.31</td>
<td>29.19</td>
</tr>
</tbody>
</table>

Fig. 1. Different properties measured in the clear state and photodarkened state (after illumination) for a 1400-nm-thick YHO film: transmittance compared to the luminous efficiency of the human eye in photopic vision [panel (a)], contact angle photographs for water, a photo of water droplets onto a clear film, as well as the same film after being illuminated under a sun-shaped mask during 1 h [panel (b)]. XPS spectra corresponding to C1s, O1s, and Y3d [panel (c)].
TABLE II. Quantification by XPS of the O, Y, and C content at the surface of a yttrium oxyhydride film in the clear and photodarkened state. Two sets of data are presented in each case. In case A the quantification has been done, taking into account levels C1s, O1s, and Y3s, whereas in B, O1s, C1s, and Y3p were considered instead.

<table>
<thead>
<tr>
<th></th>
<th>Clear state</th>
<th>Dark state</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>C (at %)</td>
<td>45.6</td>
<td>47.0</td>
</tr>
<tr>
<td>O (at %)</td>
<td>38.4</td>
<td>37.9</td>
</tr>
<tr>
<td>Y (at %)</td>
<td>16.0</td>
<td>15.2</td>
</tr>
<tr>
<td>O/Y</td>
<td>2.4</td>
<td>2.5</td>
</tr>
<tr>
<td>C/Y</td>
<td>2.9</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Fig. 1(c). The contributions of the carbonates in the O1s region seem to be negligible.

The obtained results for Y3d correspond very well to the Y2O3 stoichiometry. At the surface the samples consist of Y2O3, which agrees with our previous work [37]. The Y3d has well-resolved spin-orbit components, namely, Y3d3/2 and Y3d5/2. These components can be deconvoluted to Y2O3, with contributions at 156.6 and 158.4 eV, Fig. 1(c) [49]. An extra doublet is needed for completing the fitting, with contributions at 158.6 and 160.3 eV. In this energy range, the possibilities are Y-OH [50], yttrium carbonates [50], and Y-H [51], the latter being the best candidate, since no evidence of carbonates and hydroxides is found in C1s or O1s. There is not a remarkable change in Y3d before and after illumination.

When comparing the current XPS results with previous published data [52], it is evident that the films studied here, obtained by an optimized sputtering process [3], present higher homogeneity.

Surface-energy calculations, performed using the van Oss–Chaudhury–Good method [23,24], confirm the lower wettability through reduction under illumination of the total surface energy γotal, see Table I. The enrichment in oxygen of the surface, confirmed by XPS, reduces the Lewis sites as the surface approaches the Y2O3 stoichiometry. The nonpolar Lifshitz–van der Waals surface-energy component γAB also decreases from 38.07 to 28.57 mJ/m², while the polar acid-base component γAB decreases from 8.98 to 0.31 mJ/m² after illumination. Here γAB = 2(γ+γ−)1/2, where γ+ is the Lewis acid and γ− the Lewis base parameters of surface tension.

Hydrophobic yttrium-based oxides have been reported in the past [16,53]. In those works, as Y2O3-x coatings approached Y2O3 stoichiometries, contact angles increased [53]. This pattern is consistent with metal-to-oxygen ratios of surface studies [43]. Consequently, the enrichment in oxygen of the surface under illumination causes the light-induced hydrophobicity enhancement observed in YHO thin films. In the next section, the exchange of oxygen atoms between the film and the atmosphere, induced by illumination, is demonstrated.

B. Light-induced breathing

Photochromic yttrium oxyhydride has been obtained by the oxidation in air of reactively sputtered metallic YH2 thin films. The effect that the ambient humidity plays in this transformation is unclear. The incorporation of oxygen in the YH2 lattice causes the increase of the lattice constant a from 5.20 to 5.34 Å [2,3,54] and hence the displacement of the diffraction peaks towards lower angles. Under illumination, the lattice of the YHO films contracts back, but without reaching the original oxygen-free YH2 lattice constant [55].

After the incorporation of oxygen, NMR studies revealed that most of the hydrogen atoms in YHO remained in a local environment very similar to tetrahedral positions in YH2 [14]. Small signals, which can be attributed to mobile protons and to oxygen coordination, arise as well after air exposure.

Figure 2(a) shows a grazing incidence XRD pattern corresponding to a yttrium oxyhydride sample in its initial (clear), illuminated (photodarkened), and recovered (bleached) state. The standard diffraction peaks for YH2 and Y2O3 are also shown for comparison [Joint Committee of Powder Diffraction Standards (JCPDS) Cards No. 04-002-6938 and No. 04-002-7545].

The analysis of the XRD patterns revealed how the films undergo an accordionlike transformation: the YHO lattice contracts and expands when subjected to illumination/darkness cycles.

Our previous optical studies pointed to the reversible formation of oxygen-deficient YHO1−x, metallic domains [13] within the dielectric YHO lattice as the cause of the photochromic behavior and lattice expansion/contraction:

YHO illumination = dark, clear

Since the filling factor ff of the YHO1−x domains is predicted to be very small [13], the factor η must be η ≪ 1. Dilution of YHO1−x domains in the dielectric YHO structure is necessary to achieve higher optical absorption rather than higher optical reflectance, which is consistent with experimental observations [10,22].

Very few oxygen atoms need to be released under illumination to produce a large optical contrast. In fact, ff = 0.02 causes a drop of the visible transmittance larger than 30% [22]. In addition, not all the released oxygen atoms necessarily need to leave the sample, and the material is able to host the outdiffused O atoms [56]. This was confirmed also by XPS in Fig. 1(c). Therefore, although the effective medium approximation works very well for modeling the optical properties [22], it is very difficult to confirm the release of oxygen in the experiment.

However, we postulate that there must be some exchange of oxygen atoms under illumination/darkness between the sample and its surroundings. This exchange, as discussed before, is probably below the detection limit of most conventional techniques. To prove our hypothesis, YHO thin films were subjected to 2-h-period cycles (0.5 h illumination followed by 1.5 h darkness) inside a glovebox filled with N2. The O2 and H2O content within the glovebox was below 0.1 and 1.4 ppm, respectively. The average transmittance of the film was measured between 600 and 800 nm during cycling and plotted in Fig. 2(b). In the absence of air, the films lost part of their initial transparency in each cycle, not being able to recover fully. After 4 weeks of continuous cycling within the glovebox, the luminous transmittance Tlum of the samples decreased from 78.5% in the nonilluminated state to 26.7%.
This heavily photodarkened films were allowed to bleach in total darkness, both in air and in N₂ atmosphere (glovebox). The evolution of T_{lum} is presented in Fig. 2(c). The bleaching speed of the photodarkened samples in darkness was much slower inside the glovebox than in air. In addition, during the recovery, a series of transmittance measurements were performed during a period of 24 h, both in air [Fig. 2(d)] and in the glovebox [N₂ atmosphere, Fig. 2(d)].

The films kept in air recover their initial transparency after a few hours [T_{lum} clear, presented in Fig. 2(c) as a horizontal dashed line], while the films in N₂ recovered very little in the same period of time. Since there are no significant differences between the temperature inside and outside of the glovebox (both at ~20 °C), the data presented in Figs. 2(c)–2(e) strongly indicate that a source oxygen from the ambient is crucial for adequate recovering of the photodarkened films. The need for ambient oxygen, and possibly water vapor, is consistent with the light-induced oxygen release hypothesis summarized in Eq. (1).

The dependence on the atmospheric composition rules out other possible explanations for the photochromic mechanism, including light-induced formation of defect pairs or lattice distortion [14]. The release of hydrogen [15] (instead of oxygen) is an alternative explanation that can also be ruled out but for a different reason. In this case, the reversibility of the process would require the rehydrogenation of the film, a process that cannot take place at ambient pressure [1]. Nevertheless, if hydrogen is released, the film could bleach by the incorporation of O, eventually approaching the Y₂O₃ stoichiometry. However, this hypothesis is not supported by the x-ray diffractograms shown in Fig. 2(a) and contradicts the reversibility of the process. Besides, the very large band gap of Y₂O₃ would lead to an increase of T_{lum}. Such increments are not observed, Figs. 2(c) and 2(d).

Considering the low electronegativity of Y, the idea of oxygen being pushed out of the YHO lattice by illumination may seem counterintuitive at first. The thermodynamics and kinetics of Eq. (1) need further studies for clarification. In the next section, a preliminary theoretical model for understanding the light-induced oxygen release in YHO films is presented.

C. Theoretical considerations

The experimental evidence presented above points to light-induced oxygen exchange between the film and the atmosphere. In the present section, this question is addressed by DFT modeling (ab initio calculations using VASP 5.3.5). It is known that photochromic YHO coatings are obtained experimentally by the partial oxidation of YH₂ films in air. As discussed before, the incorporation of oxygen into YH₂ results in the expansion of the YH₂ lattice. The lattice parameter a increases, and hence the XRD peaks corresponding to YHO appear displaced towards lower angles when compared to oxygen-free YH₂, Fig. 3(a). The data presented in Fig. 3(a) corresponds to two different samples. The evolution of the XRD pattern for the same sample before, during, and after the YH₂-to-YHO transformation can be found elsewhere [3].

The oxygen intake also causes the band-gap opening. Figure 3(b) shows the experimental transmittance (T), reflectance (R), and absorbance (A) corresponding to YH₂ and compared
to photochromic YHO. YH₂ presents the optical behavior of a metal, but after the incorporation of oxygen it turns into YHO, a wide-band-gap semiconductor. The role played by the ambient humidity has not been studied yet.

Taking the crystalline structure of YH₂ as the starting point [m3-5m and space group symmetry number (SPGN) 225], we build diverse YHO lattices of stoichiometry YHₓO₃ (111), present a metallic character, whereas YHO with stoichiometry Y₂H₂O (134), as well as Y₂H₂O (111), present a metallic character, whereas YHO (216) lattice. The experimental XPS data and the calculated total density of states (DOS) at the conduction-band minimum for different YHₓO₃ stoichiometries.

The experimental XPS data and the calculated total density of states of YHO (216) are in good agreement, as shown in Fig. 2(c). The opening of a wide band gap as the oxygen atoms are incorporated in the YH₂ structure is also predicted by the ab initio calculations, Fig. 2(d). However, the model overestimates the band gap. The calculated value of 4.9 eV for YHO (216) is about 1 eV larger than the experimental band gap determined in the photochromic films by optical methods [3,22].

It should be noted that the YHO films, obtained by the oxidation of YH₂ previously prepared by reactive sputtering, are polycrystalline and multiphase in nature—note the widening of the XRD peaks of YHO when compared to YH₂ in Fig. 2(a). Therefore, the energy-band diagram of the
material most likely corresponds to a heterostructure of type II with a staggered band gap.

Assuming YHO (216) as the possible structure of photochromic yttrium oxyhydride, we can now explain the photochromic effect. The projected density of states (DOS) for YHO (216) revealed that both O and H atoms strongly contribute to the topmost valence band states. However, they are not hybridized because both H and O atoms are connected to the Y atoms independently from each other. On the other hand, the lowest conduction band is triply degenerate and corresponds to the Y atoms, Fig. 3(c). This result suggests that the light-induced O released from the film can be caused by the pseudo Jahn-Teller distortion effect: Y atoms are located at the center of the tetrahedral H and O sublattices. Under illumination, the transfer of electrons from the valence band to the $t_{2g}$ bands will turn the YHO (216) lattice unstable [59].

As the $p$ orbitals of O atoms are hybridized with the $d$ orbitals, the degeneracy of the $t_{2g}$ states can be avoided by the removal of oxygen atoms. As a result, an O-deficient unit cell with smaller lattice constant will be created. As reported by Pishtshev et al. [57], there are many O-deficient structural arrangements that can be obtained from YHO, Fig. 3.

Before illumination, yttrium cations are in the oxidation state 3+, which is the very stable state. After illumination, some (very few [13]) of the O atoms will be detached from the Y$^{3+}$ cations. Those Y atoms evolve from a 3+ to 2+ oxidation state, which is less stable. In darkness, the Y$^{2+}$ atoms oxidize back to Y$^{3+}$ by the incorporation of oxygen atoms that remained within the lattice [56], Fig. 1(c), or newly incorporated from air.

As a result of illumination, metallic domains of smaller lattice constant will be created in the YHO (216) lattice, which results in the photochromic effect and the lattice contraction observed experimentally. The material seems to be able to host the out-diffused O atoms, which in some cases can reach the surface or even leave the film as demonstrated before. After stopping the illumination, the released O atoms can return to their former positions and the initial optical transparency will be restored.

**IV. CONCLUSIONS**

When exposed to air the YH$_2$ lattice expands from 5.20 to 5.34 Å due to the incorporation of oxygen. In addition to the lattice expansion, YH$_2$ turns into YHO. YHO is transparent and photochromic. The reversibility of the photochromic effect depends on the surroundings of the films, being a source of oxygen necessary for the adequate bleaching of the samples. Therefore, the photochromic mechanism must involve oxygen diffusion and oxygen exchange between the sample and its surroundings. A consequence of the oxygen diffusion is the unusual enhancement of the hydrophobicity and the reversible lattice contraction of the YHO films under illumination. Although further studies are needed, a preliminary theoretical study points to the pseudo Jahn-Teller effect as the possible cause of this light-induced oxygen diffusion observed YHO films.

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