Surface Science xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Ferroelectrics: A pathway to switchable surface chemistry and catalysis

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ARTICLE INFO

Available online xxxx

Keywords:
Ferroelectrics
Catalysis
Photocatalysis
Switchable surface chemistry
Surface reconstructions
Novel scaling relations

ABSTRACT

It has been known for more than six decades that ferroelectricity can affect a material's surface physics and chemistry thereby potentially enhancing its catalytic properties. Ferroelectrics are a class of materials with a switchable electrical polarization that can affect surface stoichiometry and electronic structure and thus adsorption energies and modes; e.g., molecular versus dissociative. Therefore, ferroelectrics may be utilized to achieve switchable surface chemistry whereby surface properties are not fixed but can be dynamically controlled by, for example, applying an external electric field or modulating the temperature. Several important examples of applications of ferroelectric and polar materials in photocatalysis and heterogeneous catalysis are discussed. In photocatalysis, the polarization direction can control band bending at water/ferroelectric and ferroelectric/semiconductor interfaces, thereby facilitating charge separation and transfer to the electrolyte and enhancing photocatalytic activity. For gas–surface interactions, available results suggest that using ferroelectrics to support catalytically active transition metals and oxides is another way to enhance catalytic activity. Finally, the possibility of incorporating ferroelectric switching into the catalytic cycle itself is described. In this scenario, a dynamic collaboration of two polarization states can be used to drive reactions that have been historically challenging to achieve on surfaces with fixed chemical properties (e.g., direct NO_x decomposition and the selective partial oxidation of methane). These predictions show that dynamic modulation of the polarization can help overcome some of the fundamental limitations on catalytic activity imposed by the Sabatier principle.

1. Introduction

A polar surface arises when the electrical dipole associated with the bulk unit cell of a polar crystalline material has a non-zero component perpendicular to the surface i.e., $\vec{P}\cdot\hat{n}\neq 0$, where $\vec{P}$ is the bulk polarization vector and $\hat{n}$ the surface normal. The emergence of bulk polarization is a consequence of the offset between the centers of the positive and negative charges in each unit cell [1,2]. If this polarization were uncompensated, a constant electric field would develop across the material with an energy cost scaling with the thickness of the material and rapidly becoming unphysically large for thick samples. The solution is to accumulate equal amounts of compensating opposite charges ($\sigma = \pm\vec{P}\cdot\hat{n}$) on the opposing polar surfaces to cancel the interior electric field so that the energy becomes independent of thickness. This can most simply be achieved through an electronic reconstruction: electrons or holes are transferred to the surfaces to compensate the polarization charge (Fig. 1) [3–10]. Over timescales where atoms move and can migrate to or away from the surfaces, an additional avenue for compensation becomes possible: atomic reconstruction. Here, atoms are adsorbed or removed from the surfaces. These adsorbates or vacancies make available additional electronic states for electrons or holes that more favorably accommodate them compared to the energy bands of the stoichiometric surfaces. For pristine surfaces under UHV, the adsorbates are typically species found in the bulk, for example oxygen anion adsorption on the positive surfaces of polar oxides, while under ambient conditions a range of foreign species must also be considered. Such defects then accept the electrons or holes and lower the total energy of the surface, becoming ions in the process (in some cases charged species may adsorb directly). Thus, the net effect of atomic reconstruction is to add ions to the surface that balance the polarization with a surface charge density of opposite sign and cancel the electric field inside the material. It is worthwhile to note that there are scenarios where the polarization may not be entirely compensated. For example, ultra-high vacuum (UHV) can limit atomic reconstructions through adsorption while optical and thermal excitations in large bandgap ferroelectrics can be insufficient to fully compensate the polarization through electronic reconstruction [11–13]. Another mechanism by which ferroelectric surfaces may avoid reconstruction is through the formation of nanodomains of alternate polarization which can eliminate the net polarization [14].

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http://dx.doi.org/10.1016/j.susc.2015.10.055
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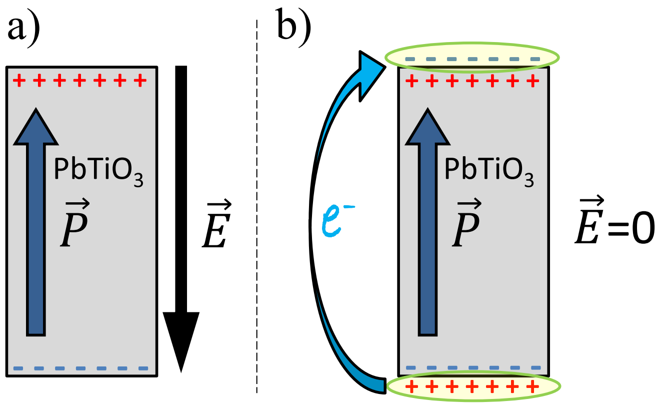

Fig. 1. Schematic illustration of two scenarios for a ferroelectric surface. a) Unphysical scenario: a large depolarizing electric field exists across the entire material created by the uncompensated surface charges stemming from ionic displacements along the polarization direction. b) Electronic reconstruction by electrons or holes for positive or negative polarization $\vec{P}$ which results in zero net electric field inside the material.

Polar surfaces almost always minimize their energy through some variety of atomic reconstructions rather than through purely electronic reconstructions [3,15–30]. These atomic reconstructions change the stoichiometry relative to the bulk termination which, in principle, can change the surface chemistry. Also, while the compensating charges eliminate the thickness-dependent component of the dipole, surface dipoles remain which can affect adsorption of polar molecules [31]. Ferroelectrics are a class of materials that have a spontaneous electric polarization vector (an order parameter) whose direction can be switched using an electric field and whose magnitude is temperature-controlled through the pyroelectric effect [32,33]. The modifications of ferroelectric surfaces due to the compensation of the surface charge density via adatoms, vacancies, surface dipoles and changes in surface electron density can all, in principle, alter the surface chemistry. Hence, ferroelectrics are promising candidates to achieve switchable and controllable surface physics and chemistry in which certain reactions can be turned on, off, or tuned.

Since the mid 20th century, the intriguing possibility of dynamically controlling surface chemistry and enhancing catalytic properties has turned ferroelectric and polar materials into the subject of numerous studies. Starting in 1952, Parravano observed anomalies in CO oxidation rates over ferroelectric sodium and potassium niobates near the Curie temperature of these materials (the second order transition temperature when the polarization vanishes) [34]. Next, in the 1960s, Stadler demonstrated that ferroelectric polarization can change the physical properties of supported metal films [35,36]. The subject received renewed attention in the 1980s when Inoue et al. studied the effect of the substrate polarization on the catalytic activity of supported metals and found higher CO oxidation rates for negatively poled surfaces, which they attributed to weaker CO adsorption for metal supported on the positively poled surface [37,38]. In the same timeframe, dramatic effects of the polarization direction on adsorption on polar, but not ferroelectric, materials were demonstrated [39,40]. Using Temperature Programmed Desorption (TPD) measurements to study the adsorption of oxygen-containing molecules that possess strong dipole moments, such as formaldehyde and formic acid, on polar ZnO surfaces, Akhter et al. showed strong interactions with the Zn-polar (0001) face, a weaker interaction with a non-polar face, and only a weak interaction with the O-polar $(000\bar{1})$ face [39]. Vohs et al. also studied ZnO polar surfaces using TPD and X-ray Photoelectron Spectroscopy (XPS) and showed that the Zn-polar crystal face readily oxidized both formic acid and formaldehyde while the O-polar face was unreactive [40].

The photocatalytic properties of ferroelectrics and polar materials have also attracted significant attention in the scientific community [41–60]. As far back as 1986, Inoue et al. studied photoassisted water decomposition on lead zirconate titanate (PZT) ceramics. In these experiments, 10–40 times higher H_2 production rates were observed for positive relative to negative polarization [42]. The main underlying mechanism was determined to be the polarization-dependent band bending close to the ferroelectric surface that facilitates the separation of the electron-hole pair and, depending on the polarization direction, directs either electrons or holes to the surface. Thus, in positive polarization, enhanced electron transfer to the surface promotes the hydrogen evolution reaction. A photocatalyst with a semiconductor/metal/ferroelectric structure was studied in which the semiconductor (TiO_2) exhibits a higher efficiency for hydrogen formation for positive polarization in contrast to negative polarization [43]. In succeeding work on the ferroelectric semiconductor lead strontium zirconate titanate ($Pb_{0.95}Sr_{0.05}Zr_{0.53}Ti_{0.47}O_3$), the difference in hydrogen evolution activity on the positive compared to the negative surface was increased by more than two orders of magnitude [44]. In 2001, Giocondi et al. studied photochemical oxidation and reduction reactions on the surface of ferroelectric $BaTiO_3$. For UV irradiation under aqueous solutions containing dissolved Pb^{2+} or Ag^+ cations, they observed accumulation of the oxidation product PbO_2 and the reduction product Ag on opposite polarization domains in patterns that reproduced the underlying ferroelectric domain structure. This demonstrated the ability of the ferroelectric to preferentially direct photogenerated electrons or holes to the surface depending on the polarization direction [61,62].

Building on the results of Giocondi et al., the novel method of ferroelectric lithography was proposed in which ferroelectrics are utilized to fabricate multicomponent nanostructures (oxide substrates, metal nano-particles and organic molecules) [63–69]. In this method, ferroelectric polarization in the substrate is manipulated to control local electronic structure and chemical activity and is patterned with electron beams or probe tips. By using photo reduction from aqueous solution, metal nanoparticles are deposited on predefined locations (see Fig. 2). Organic molecules can then react selectively on these nano-particles. This process can in principle be repeated to develop even more complex structures.

All ferroelectrics are necessarily pyroelectric so that their polarization magnitude is temperature dependent [70,71]. Hence, heating or cooling a ferroelectric changes the balance of the surface compensating ions and surface polarization charges; as a result, the surface can temporarily find itself with extra charges for some time before it relaxes due to molecular adsorption/desorption or cancellation by the material's free carriers. As explained by Yun et al. [31], this leads to a sizable change in the surface dipole moment that can change surface chemistry. This effect is most noticeable in ferroelectrics with lower free carrier densities which strongly prefer external screening by adatoms (vacancies). This phenomenon has been exploited to create self-focusing, spatially stable, high energy (170 keV) electron beams using $LiNbO_3$ crystals in dilute gases [72], and to achieve "tabletop" nuclear fusion [73–75]. The basis of these experiments is the creation of a strong electric field near the ferroelectric surface which results from temporarily uncompensated charges on the surface of the ferroelectric created by heating or cooling [76–83].

The seminal works briefly outlined above have motivated many fundamental studies on ferroelectrics and ferroelectric-supported thin films in recent years. In addition to many experimental studies, the development of better computational facilities, algorithms, software packages [84] and ab initio electronic structure methods, especially Density Functional Theory (DFT) and its derivatives, [85–90], has led to a considerable number of theoretical studies in this field. Below, we review prominent recent experimental and theoretical results in the field of ferroelectric surface chemistry and provide an outlook on avenues that may potentially further advance this field. In particular, a strong potential benefit of ferroelectrics for catalysis can be their ability to deliver surfaces with dynamically switchable and tunable chemical properties. These systems may enable the realization of efficient processes for

Please cite this article as: A. Kakekhani, et al., Ferroelectrics: A pathway to switchable surface chemistry and catalysis, Surf. Sci. (2015), http://dx.doi.org/10.1016/j.susc.2015.10.055