Review

Polarization boosted catalysis: progress and outlook

Lin Ju[1], Xiao Tang[2], Liangzhi Kou[3]

[1]School of Physics and Electric Engineering, Anyang Normal University, Anyang 455000, Henan, China.
[2]College of Science, Institute of Materials Physics and Chemistry, Nanjing Forestry University, Nanjing 210037, Jiangsu, China.
[3]School of Mechanical, Medical and Process Engineering, Queensland University of Technology, 2 George St, Brisbane City QLD 4001, Brisbane, Australia.

Correspondence to: Prof. Liangzhi Kou, School of Mechanical, Medical and Process Engineering, Queensland University of Technology, 2 George St, Brisbane City QLD 4001, Brisbane, Australia. E-mail: liangzhi.kou@qut.edu.au

Abstract

Polarization has a significant impact on chemical reactions, as demonstrated by recent research of photo-/electrocatalytic water splitting, electrocatalytic CO_2 reduction, water treatment, dye degradation and so on. This review summarizes the fundamental influence of polarization on the physical/chemical properties of catalysts and discusses polarization-dependent catalytic processes. Based on the research progress of polarization-modulated chemical reactions, we draw the conclusion that the control of polarization can be used to adjust the reactivity and selectivity of various catalytic reactions by tuning the miscellaneous fundamental properties of polarized catalysts. At the end of the review, the future research challenges are also discussed, including the ultrafast reversal of polarization, the magnetic-field control of chemical reactions through the magnetoelectric effect and in-plane polarization.

Keywords: Polarization reversal, electrocatalysis, water splitting, photocatalysis

INTRODUCTION

Chemical catalysis, which can convert reactants into desirable chemical products, has attracted extensive research attention in recent years due to its potential for alleviating air pollution and the urgent energy crisis. Numerous catalysts have been proposed for CO_2 and N_2 reduction, water splitting and so on. However, the catalytic activities and efficiencies of these catalysts remain far from the required standards for

practical applications due to the intrinsic constraints from the Sabatier principle and the adsorption scaling relationship, which can be evaluated with scanning probe microscopy by visualizing the surface properties and localized electrochemical activity[1].

For non-polarized catalysts, external stimuli, such as strain deformation, surface passivation and electric fields, have been proposed to improve catalytic performance but the upper limit of efficiency imposed by the linear scaling relation cannot be lifted. In contrast, in polarized materials, such as ferroelectrics, pyroelectrics, piezoelectrics and their associated composites materials (see Figure 1A), the adjustment of polarization is considered as one of the most promising methods to break the upper limit of efficiency and boost catalytic activities. Similar to the influence of external electric fields on the gas adsorption/desorption behavior of field-effect transistor sensors, which is realized by adjusting the electron transfer between the gas and substrate at the interface[2-4], the electric spontaneous polarization in polarized catalysts can tune the adsorption behavior of reactants, intermediates and products in the same manner. It has been predicted that the adsorption intensity of ionic species at the catalyst surface can be incremented by polarization of the material, where the adsorption behavior of polar species is dependent on the polarization direction[5-7]. In addition to changing the interfacial electron transfer, the polarization transformation inevitably results in reconstruction, namely, the rearrangement of the electric domain orientation. This provides an opportunity to break the adsorption scaling relationship. Thus, the physicochemical reactivity is dependent on the structural domain orientation and the surface polarization in the potential of the material[8-10], which can adjust the electro- and photocatalytic performance.

In addition to the remarkable impact on the adsorption behavior, the electron-hole separation of catalytic materials is also significantly influenced by the electric spontaneous polarization[11,12]. With regards to photocatalysis, the polarization allows for good separation of the light-excited charge carriers to optimize the efficiency of catalysis[13,14], as demonstrated in organic photovoltaics, where ferroelectric polymers were used to promote charge separation and improve the overall efficiency of the cell[15,16]. Similar phenomena were observed in the polarization-modulated photocatalytic activation and photovoltaic conversion of tetragonal $BaTiO_3$ (BTO)[12,17]. The chemical interaction between the reactants and the catalyst in electrocatalysis can be influenced as a result of polarization[18]. For example, poled $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) was found to be a superior catalyst for the oxygen evolution reaction (OER) with better performance than that of the unpoled material[19]. A positive polarization causes the Tafel slope to decline from 85 to 39 mv/decade, with a threefold increase in mass activity. The intensely improved OER activity of the polarized specimen can be ascribed to the proper Schottky barrier and flat-band potential between the electrolyte and electrode, which govern the OER performance and can be tuned by remnant polarization. In Janus transition metal dichalcogenides, an enhancement in catalysis responsiveness and selectivity was found, as their surface stoichiometry, reaction activation and adsorption intensity were dramatically regulated by their polarization[20].

As well as adsorption behavior and charge separation [Figure 1B], some other physical and chemical properties of catalytic materials are also remarkably influenced by electric spontaneous polarization and therefore enable tunable chemistry on poled surfaces[21,22]. Inspired by the promising potential of polarization-driven catalysis, in the present review, we briefly highlight recent research progress in this important field. The strategies to control and characterize polarization are first introduced. We then review the research progress for the polarization-driven catalysis of water splitting, CO_2 reduction, dye degradation and redox reductions. Further challenges and possible research directions are discussed in the final section. This review provides an overview of polarization-driven catalysis and is anticipated to inspire experimental demonstrations in the near future.
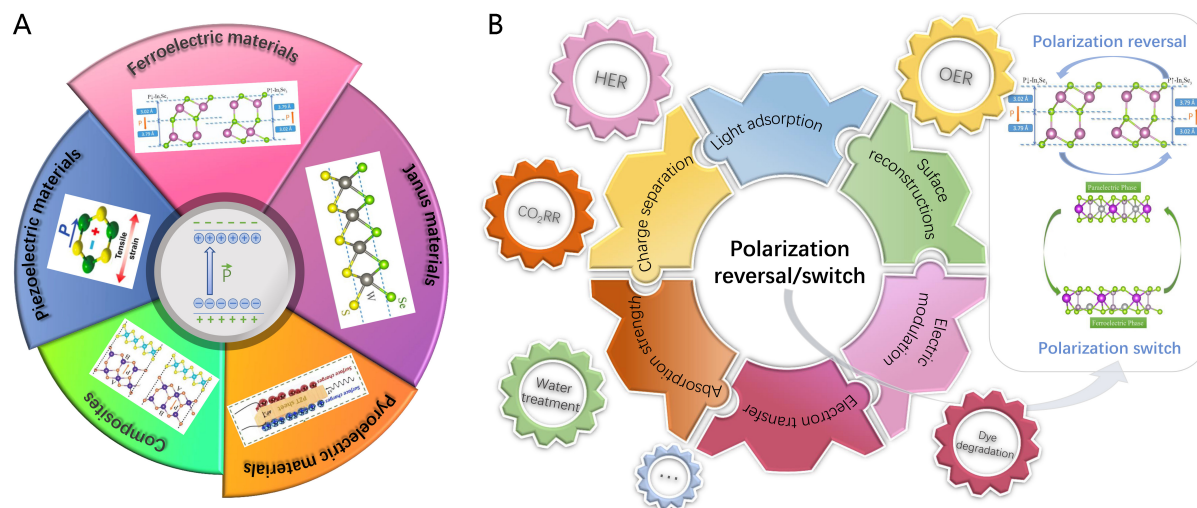
Figure 1. Schematic illustration of (A) polarized materials and (B) polarization-driven catalysis involving polarization-dependent fundamental properties and catalytic reactions.

STRATEGIES TO CONTROL AND CHARACTERIZE POLARIZATION

Ferroelectric, piezoelectric and pyroelectric materials are traditional polarized materials. In ferroelectric materials, there is a spontaneous polarization that can be reversed or reoriented with an external electric field[23]. Similarly, a voltage will appear between their two ends of the piezoelectric materials, when they are subjected to pressure[24]. With regarding to pyroelectric materials, their internal spontaneous polarization temporarily changes with a change in temporal temperature[25]. Consequently, polarization (including its magnitude and direction) in these materials can be controlled by external electric fields[26-28] or other physical stimuli, such as temperature[29], force[30-32], ultrasonic waves[33] and optical pulses[34,35]. According to X-ray photoelectron spectroscopic binding energy shifts, charge-sensitive states on materials can be derived[36]. Therefore, X-ray photoelectron spectroscopy is capable of characterizing the polarization of surfaces of free ferroelectric thin films[37-42].

Recently, surface chemical engineering in specific chemical environments has been utilized to control the polarization orientation in experimental works[43-46]. Since surfaces are freely available for structural reconstruction, they can be in chemical equilibrium in a managed environment. Polarization in bulk can be varied according to the compensation of surface ions, similar to the case with an applied voltage. This can be explained by the fact that, as shown in Figure 2A-C, when a positive/negative charge is applied to the top of the thin film, the double-well free energy becomes unsymmetrical. The polarization orientation is inverted if the surface charge has the same polarity as the bound charge[47]. Hereinafter, some recent research works are presented for controlled polarization by surface chemical engineering.

BTO films

The adsorption of water was found to have a significant effect on the out-of-plane polarization of ultrathin films according to both theoretical and experimental results[43,48]. For example, Deleuze *et al.*[48] found that water adsorption has the ability to reverse the polarization of ultrathin BTO films. Interestingly, different behaviors were observed on opposite surfaces. Water molecules were dissociated spontaneously at the surface of the BaO end and the downward polarization domain was stabilized, irrespective of the original polarization. In contrast, at the TiO_2-terminated surface, the interference of water with the TiO_2-terminated surface always results in a domain that has an upward polarization. From theoretical studies of BTO (001) plates grown epitaxially on a Pt (001) surface, it was found that the stability of the ferroelectric plates could
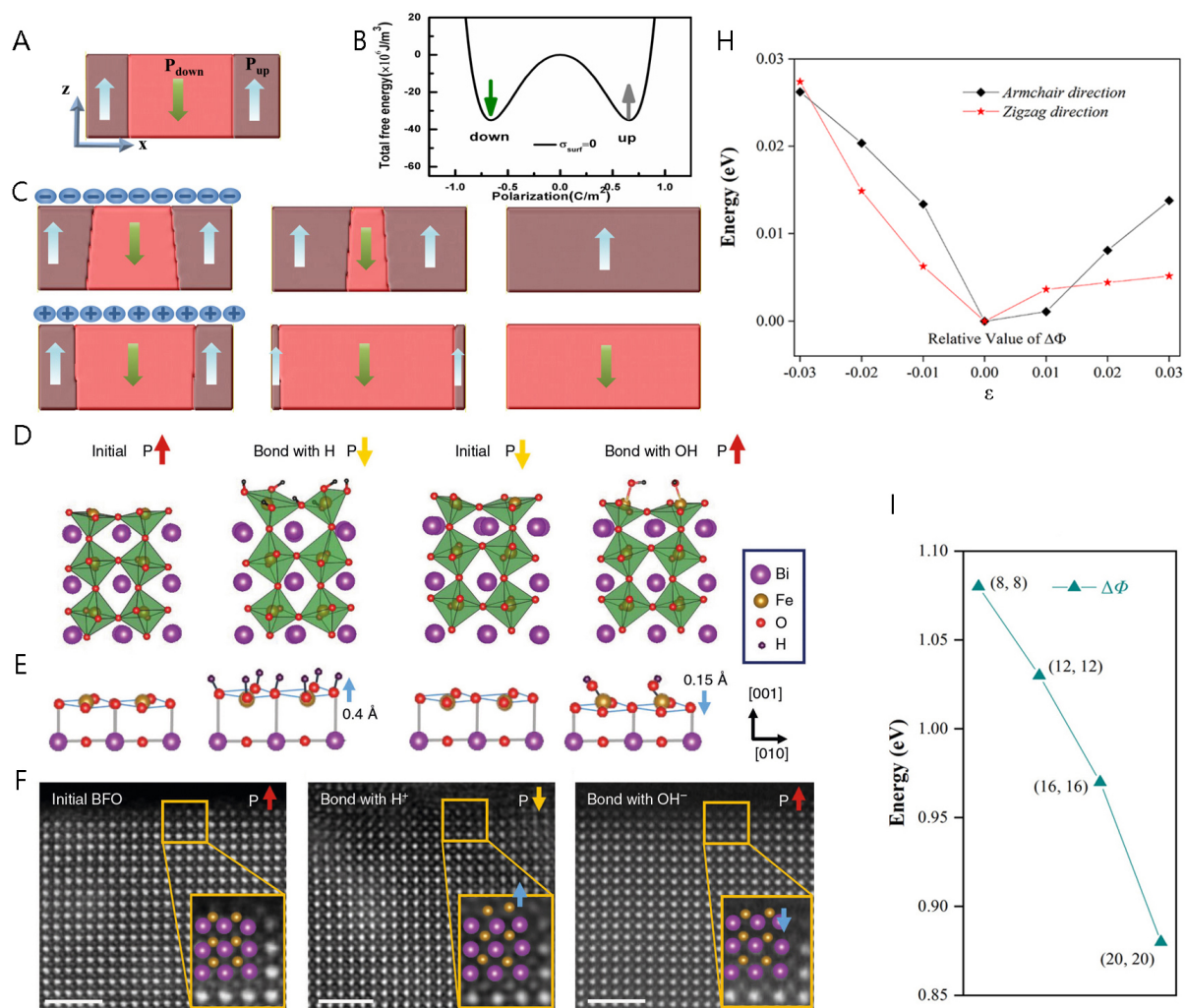
Figure 2. (A) Initial domain structure of 30 nm thick PZT thin film without surface charge and (B) its corresponding double-well total free energy. (C) Evolution of domain at different densities of positive and negative surface charges[47]. (D) Polarization of BFO switched from upward/downward to downward/upward after adsorption of four H and two OH radicals. (E) Density functional theory simulations showing displacement of Fe and O atoms along the Z-axis of the BFO surface with the adsorption of four H and two OH. (F) Scanning transmission electron microscopy images of BFO thin film, including the pristine state and the case of contact with Milli-Q water and an acidic solution[43]. (G) Variations of electrostatic potential difference as a function of armchair and zigzag strains in WSSe monolayer[20]. (H) Variations of electrostatic potential difference as a function of size for WSSe armchair nanotubes[55]. PZT: $Pb(Zr_{0.2}Ti_{0.8})O_3$; BFO: $BiFeO_3$.

be improved compared to paraelectric plates. Because of the Pt-O bond, the local polarization of the $Pt/BaTiO_3$ interface was altered and that of the central unit cell increased[49].

$BiFeO_3$ films

In addition to BTO films, similar phenomena have also been found in $BiFeO_3$ (BFO). The downward ferroelectric domains are spontaneously inverted to the original upward state when an initially upwardly polarized BFO film (5×5 μm^2) with downward ferroelectric domains is introduced to a drop of aqueous solution (Milli-Q water, pH = 7), as verified from in-situ piezoresponse force microscopy images[50]. Tian *et al.*[43] reported that the reconstructed chemical bonding on the surface of ferroelectric BFO in an aqueous solution results in reversible polarization switching, due to the adequate formation of chemical bonds on its surface that is polarization selective. As shown in Figure 2D, OH^- and H^+ are preferentially

adsorbed by the BFO surface with downward and upward polarization, respectively. First-principles simulations showed that when H and OH come into contact with O and Fe in the energetically favorable FeO_2 plane on the BFO surface[51], ionic reactions occur to build M-O-H bonds, resulting in the atomic displacement of the Fe ion relative to its original state, as shown in Figure 2E. Structural analysis using annular bright-field high-resolution scanning transmission electron microscopy around the BFO surface in Figure 2F further confirms this surface atomic displacement and it could be obviously observed that the Fe atoms move upward (downward) as soon as they are exposed to an acidic (water or alkaline) aqueous solution. This drastic atomic displacement suggests a directional reversal of the polarization of the surface.

$Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films

For ferroelectric-based heterojunctions, the orientation of the polarization depends on the doping or charge state of the substrate, so the polarization state can be modified via the substrate[52]. For thick layers (> 200 nm), a poor compensation of the depolarization field of $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films is reported to form 180° domains where the pyroelectric coefficient decreases strongly[53].

Janus transition metal dichalcogenides

Janus transition metal dichalcogenides, as new polarized materials, have attracted intensive research interest due to their promising applications in energy conversion[54]. These materials have intrinsic polarization caused by structural asymmetry, which can improve the spatial separation between carriers. Intriguingly, in our recent work, we found that both tension and compression strain is able to enlarge the polarity of layered Janus transition metal dichalcogenides, according to the variation of the electrostatic potential difference between the two respective surfaces with the external force [Figure 2G][20]. When they are rolled into nanotubes with a small diameter, the polarization can also be enhanced, as illustrated in Figure 2H[55].

POLARIZATION-DEPENDENT CATALYTIC REACTIONS

As discussed above, catalytic performance is affected by polarization due to the synergistic effects of multiple factors, including light adsorption, charge separation, band alignment, adsorption strength and so on. The impact of polarization should be universal, as has been demonstrated from photo- and electrocatalytic works. In the following sections, we present several typical research works on catalysis and emphasize the role of polarization.

Water splitting and wastewater treatment

Hydrogen is expected to make a significant contribution as a near-future source of renewable energy because of its high energy density and low greenhouse gas emissions, thereby making it an attractive alternative to fossil fuels. At present, water splitting is the main approach for H_2 generation. Furthermore, wastewater treatment also plays a vital role in the sustainable development of natural resources, including the protection of public health and the environment. For both water splitting and wastewater treatment, the polarization of catalysts is an important factor in determining their performance. Tunable polarization (in both magnitude and direction) enables the switching of surface chemistry[7,11,56,57]. The underlying reason for this is that the polar surfaces of catalysts have different electrostatic energies, which facilitate the attraction of positively polarized surfaces to negative radicals and negatively polarized surfaces to positive radicals[9].

Water splitting: For electrocatalytic water splitting, theoretical work based on PTO showed that the splitting of water into oxygen and hydrogen is possible by thermally cycling a ferroelectric above and below its Curie temperature (T_c) when it is exposed to water molecules[57]. This hypothesis has been demonstrated by using pyroelectricity as an extrinsic charge source to generate a potential difference for water splitting[58,59]. Recently, it was revealed that hydrogen generation is possible merely by placing a pyroelectric material in direct contact with water and applying a cycle of heating and cooling[60,61]. Thuy Phuong *et al.*[62]

reported enhanced water splitting via piezocatalysis in $Ba_xSr_{1-x}TiO_3$ by ultrasonic excitation at its T_c, as shown in Figure 3A. This material displays the maximum and most pronounced piezoelectric constraint at around T_c (see Figure 3B), which is beneficial for raising the electronic quantity for H_2 generation[62]. Due to the synergistic effect of polarization-induced advantages (decreased flat-band potential and increased Schottky barrier height), the OER performance of poled BNT was found to exceed that of unpoled BNT[19]. Furthermore, Kim reported the conceptual proposal of an ON-OFF toggleable HER catalyst with two-dimensional ferroelectric In_2Se_3. As displayed in Figure 3C, with vertical stacking of the basal plane of In_2Se_3 on top of cobalt, they found that the reversible polarization switching from polarization down to up in the In_2Se_3 monolayer could convert the HER activation of the heterostructure to the "ON" ($\Delta G_{H^*} < 0.2$ eV, ΔG_{H^*} is the free energy of atomic hydrogen adsorptions) and "OFF" ($\Delta G_{H^*} > 0.2$ eV) states, respectively. Furthermore, convertible HER activity was also found even with the stacking of In_2Se_3 bilayers on Co plates[63].

For photocatalytic water separation, polarization may significantly affect the reaction efficiency because, as recently demonstrated, the electronic properties allow for good tuning by ferroelectric polarization[64-68]. The two-dimensional M_2X_3 (M = Al, Ga, In; X = S, Se, Te) family that has emerged recently, together with Janus transition metal dichloride, has proven to be suitable for overall water splitting, owing to the presence of vacuum level differences and redox potential shifts on the two respective surfaces. The polarization itself may result in separation in the space of the photogenerated carriers[69]. Moreover, an intrinsic dipole contributed to alleviating the band gap (1.23 eV) limitation on water splitting under the reaction mechanism suggested by Li *et al.*[70]. This implied that there is also an opportunity for polar semiconductors in the narrow band gap to be compatible with the redox level of water, which makes it possible to use visible or even infrared light for photocatalytic water splitting. The improvement of solar to hydrogen efficiency comes mainly from the intrinsic spontaneous polarization, according to the analysis above.

More interestingly, on the basis of the oxidation reduction potential analysis, we found that the photocatalytic activities of $AgBiP_2Se_6$ monolayers can be well adjusted by the ferroelectric-paraelectric phase transition[71]. In particular, the FE phase with a higher oxidizability is considered as a promising photocatalyst for water oxidation, while the PE phase with stronger reducibility is more suitable for the hydrogen reduction reaction. It was also found that the ferroelectric switch can also regulate the exciton binding energy of ABP_2X_6 (A = Ag, Cu; B = Bi, In; X = S, Se) monolayers, i.e., the exciton binding energy is always smaller in the PE state than in the FE state[71].

In addition, Ortiz *et al*[72]. reported that the efficiency of hydrogen production using hot electrons produced on plasmon particles was increased by nearly an order of magnitude for gold nanorods (AuNRs) deposited with ferroelectric PTO particles in comparison with metallic Pt-AuNR catalysts. The underlying reason for this was that the remnant electric dipole moment of the PTO particles made the hot charges in the Pt-AuNR-PTO composite inject into the PTO region to drive the photocatalysis reaction, as presented in Figure 3D[72].

Water treatment: Membrane techniques are widely applied in wastewater treatment. However, for most commercial membranes, there is a trade-off between selectivity and permeability[73,74]. Pu *et al.*[75] demonstrated that charged membranes, realized by assembling charged BTO nanoparticles with interfacial polymerization, could solve this issue. They found that, polarized ferroelectric membranes (TFN-mBTO-E) exhibit increased permeability in comparison with common membranes and unpolarized TFN-mBTO membranes (2.4 and 1.5 times) and a ~97% favorable rejection rate as a result of both a hydrophilicity enhancement and a surface electronegativity increase due to the ferroelectric charge (see Figure 3E).
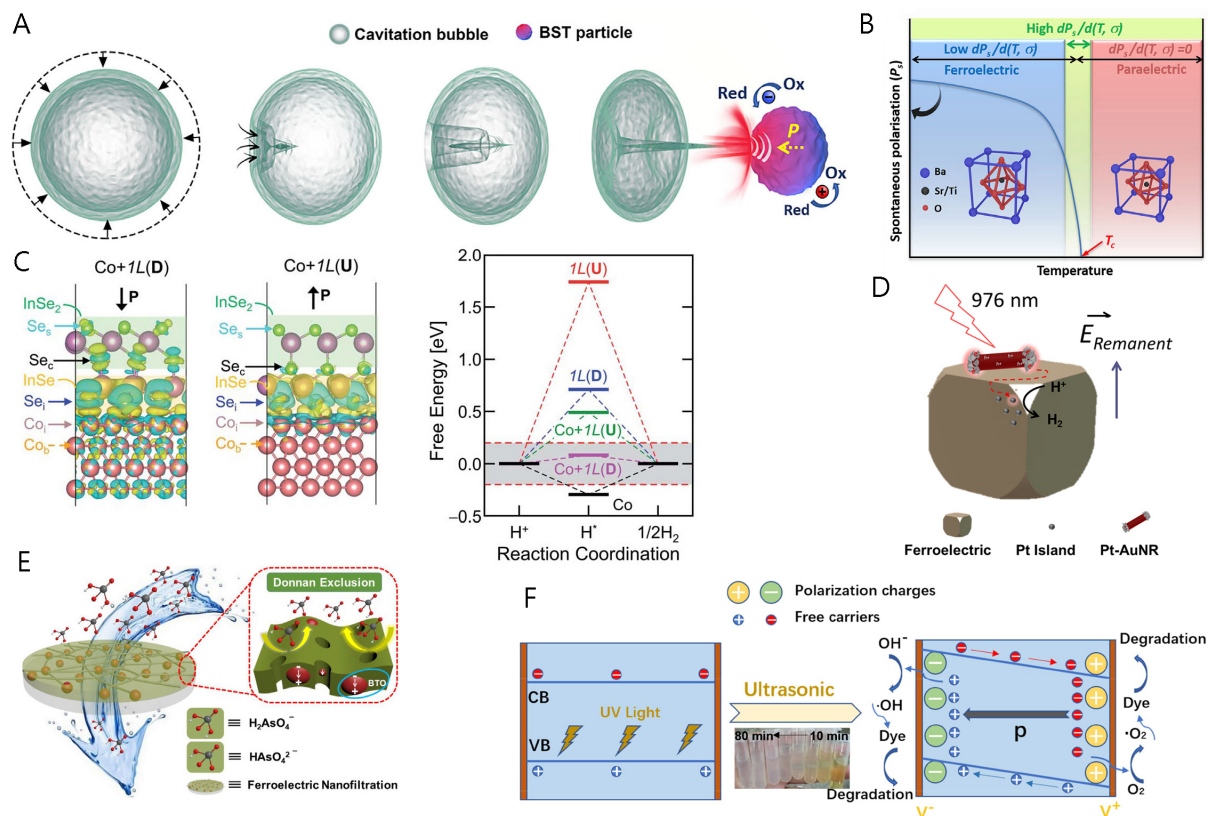
Figure 3. (A) Schematic of cavitation effect of $Ba_xSr_{1-x}TiO_3$ ferroelectric particles in the presence of ultrasound. (B) Effect of Curie temperature T_c on polarisation[62]. (C) Hydrogen evolution reaction (HER) free energy diagrams at zero potential over diverse Co-In_2Se_3 heterojunctions. (D) By binding AuNRs with ferroelectric PTO pellets, which possess greater remanent electric dipole moments, the hot charges produced on the plasma particles are able to pump into the ferroelectric material and actuate the photocatalytic HER[72]. (E) Ferroelectric membrane for water purification to reject arsenic[75]. (F) Schematic of the markedly improved piezoelectric photocatalytic ability of BTO nanowires to degrade the environmental aspects of an organic dye[82]. T_c: Curie temperature; AuNRs: gold nanorods.

Ferroelectric membranes offer a new route to concurrently boost water flux and arsenic rejection[75].

Organic dye degradation

The built-in electric field in a polarized material caused by the local charge permits the spatial separation of free electron-hole pairs that react further with solubilized oxygen molecules and water in the decomposition of organic polymers. Various polar materials, such as $Pb(Zr_{0.52}Ti_{0.48})O_3$, ZnO, $NaNbO_3$, MoS_2 and BTO, as catalysts for water splitting and organic contaminant decomposition, have been widely explored[76-81]. Liu *et al.*[82] reported that ultrasonic vibrations can enhance the catalytic activity of BTO nanowires for degrading organic dyes via integrating photocatalysis with the piezoelectric-like effect. Ultrasonic vibrations not only introduce the production of free charge carriers but also generate an internal built-in electric field (polarized charge formation on the catalyst surface) to retard the recombination rate between holes and electrons. As a result, more carriers migrate to the surface of BTO nanowires to form ·OH and O_2^- radicals [Figure 3F]. Thus, the piezoelectric-photocatalytic synergy led to excellent and effective dyestuff degradation. The degradation rates were 1.28 and 2.24 times higher than those of piezoelectric catalysis and photocatalysis alone, respectively[82].

In a polarized system of C/Bi/Bi_2MoO_6, the non-centrally symmetric arrangement of ionic groups renders one edge (C^+ area) with a positive charge and the other edge (C^- area) with a negative charge, thereby

creating a self-polarized field from the C^+ to C^- areas. Following an electrolysis analysis, a uniform distribution of the polarization field was found with e^- and h^+ on the C^+ and C^- edges, respectively, which facilitated the separation of bulk charge. Profiting from the effect of polarization, a significant improvement in the photocatalytic performance of the material was achieved[83]. A study of the impact of polarization on the photodegradation of Rhodamine B from $KNbO_3$ (KNO) nanoparticles was conducted by Fu *et al.*[84]. High-quality KNO samples can be polarized under varying electric fields and the measured changes of piezoelectric coefficients from XRD clearly indicate the increased strength of ferroelectric polarization. Because of the strengthened internal field, the photoluminescence lifetime and photodegradation rate after the polarization were significantly enhanced. These are the possible factors to explain the enhanced photocatalytic behavior of the polarized KNO samples in terms of the increased internal electric field.

Polarization-controlled CO_2 reduction

Escalating worldwide fuel costs and their negative environmental impact are the main human development priorities of the 21st century[85-91]. As a result of the overuse of shale fuels, there are serious threats to human health from the greenhouse effect. The development of technologies that can turn greenhouse gases (i.e., CO_2) into renewable and environmentally clean sources of energy is greatly desirable.

As shown in Figure 4A, a sustainable electrochemical approach to reduce CO_2 to carbon-based products using renewable electricity as an input has drawn significant research interest[86]. Experimentally, various materials, such as elemental metals, metal oxides/hydroxides, alloys, carbon-based materials, chalcogenides, metal/covalent organic frameworks and molecular catalysts, have been studied for the electrochemical CO_2 reduction reaction (eCO_2RR)[92-97]. Although significant progress has been made in recent years, the eCO_2RR systems currently available are not sufficient for industrial demands due to large overpotentials and poor product selectivity[98]. Reliable electrocatalysts and effective control means are essential for accelerating the sluggish eCO_2RR and improving product selectivity.

Recently, through first-principles simulations, six ferroelectric catalysts consisting of transition metal atoms anchored on In_2Se_3 monolayers were determined. As shown in Figure 4B, their catalytic properties for the eCO_2RR can be governed by a ferroelectric switch, which can tune the occupation and d-band center of the supported metal atoms. The activation related to polarization permits an effectively controllable limiting potential, reaction pathway and final product. As displayed in Figure 4C, the most favorable path for the eCO_2RR on the surface of Nb@In_2Se_3 with downward polarization is $CO_2^* \rightarrow OCHO^* \rightarrow OCH_2O^* \rightarrow HOCH_2O^* \rightarrow O^* \rightarrow OH^* \rightarrow H_2O^*$, producing methanol with a limiting potential of 0.64 eV. In sharp contrast, on the surface of Nb@In_2Se_3 with upward polarization, the eCO_2RR path is $CO_2^* \rightarrow OCHO^* \rightarrow HOCHO^*$, producing methanoic acid with a limiting potential of 0.58 eV. Intriguingly, the ferroelectric switch could even reactivate the catalysis CO_2 reduction stuck on Zr@In_2Se_3. As shown in Figure 4D, due to the extremely strong binding strength of the intermediate HOCHO*, a further hydrogenation step is forbidden on Zr@In_2Se_3 with upward polarization (ΔG = 2.33 eV). When the polarization direction is reversed from up to down in this step, the barrier greatly decreases (ΔG = 0.61 eV), reactivating the catalytic reduction process. The reasonably low limiting potential and distinctive ferroelectrically manageable CO_2 catalytic properties on the atomically dispersed transition metal on In_2Se_3 significantly differentiates it from conventional single-atom catalysts and creates a pathway to improve the catalytic efficiency and selectivity for highly efficient and well-controlled electrochemical eCO_2RRs[99].

General redox reactions

Photoreduction of Ag^+ and photooxidation of Pb^{2+}: The spontaneous polarization of domains in ferroelectric materials has been employed to separate photogenerated holes and electrons in space, thereby decreasing recombination and enhancing the photochemical reaction efficiency. Song *et al.*[100] investigated
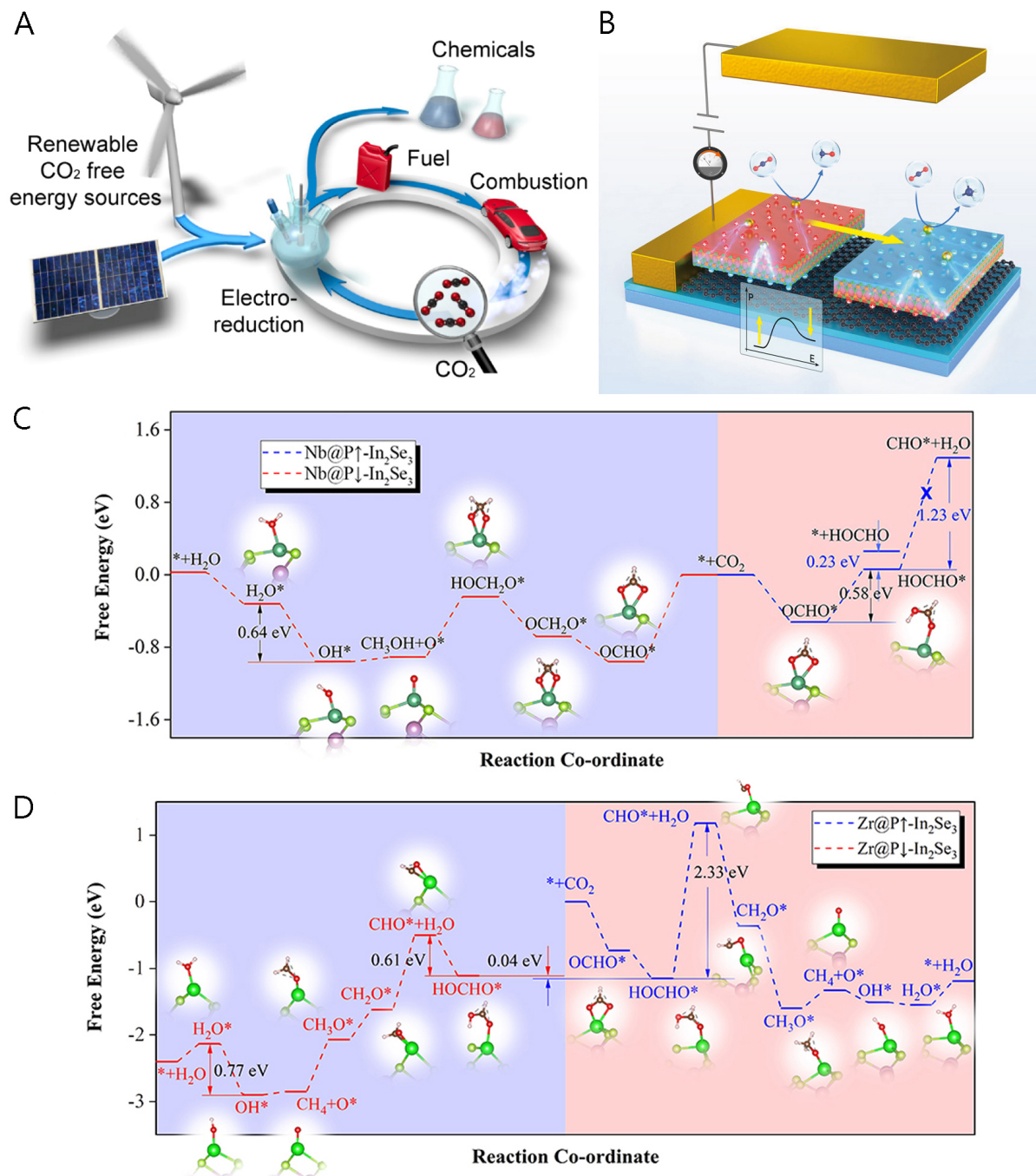
Figure 4. (A) CO_2-neutral energy cycle through electrochemical reduction using renewable electricity sources[86]. (B) Schematic diagram of ferroelectric controllable eCO_2RRs. The α-In_2Se_3 monolayer anchored by a single metal atom is positioned across the electrodes for the reversal of polarization and controlled catalysis, which is tuned by reversing the bias orientation[99]. Free energy curves following the minimum energy route at 0 V (*vs.* RHE) for the eCO_2RRs on (C) Nb@In_2Se_3 and (D) Zr@In_2Se_3. *Stands for the active site. The inset illustrates the optimal shape of the intermediate. The shaded area in pink (light purple) denotes the catalytic reaction when the polarization is up (down)[99]. eCO_2RRs: Electrochemical CO_2 reduction reactions.

the influence of polarization on the photochemical reactivity for Ag⁺ photoreduction and Pb²⁺ photooxidation on a BTO (001) surface. By measuring the photochemical reactivity of domains with different polarization directions, they found that the reduction reactivities of domains with the

perpendicular polarizations were about three times greater than the one parallel to the surface, while only the oxidation reactivities of domains with perpendicular polarizations were reactive. They concluded that for the photoreduction of Ag^+, the size of the out-of-plane polarization was not as important as its sign, whereas for the photooxidation of Pb^{2+}, not only the sign, but also the size of the polarization was important[100].

Direct oxidation of CH_4 to CH_3OH: Based on density functional theory simulations, Kakekhani *et al.*[11] investigated the polarization associated interaction between stoichiometric Pb-terminated PTO and methane. While the reduced surface with the positive polarization does not interact with CH_4, the oxidized surface with the negative polarization, intensively reacts with CH_4 and alters CH_4 oxidation to CH_3OH. An energy barrier of ~1.1 eV is calculated for this reaction. However, the binding energy of CH_3OH with the residual surface is negligible (< 0.1 eV), indicating that it can easily desorb. Therefore, it is feasible to oxidize CH_4 to CH_3OH via cycled polarization of the PTO surface.

SO_2 oxidation to SO_3: In addition to CH_4, the oxidation of SO_2 is also polarization-dependent, as evidenced by the interaction between SO_2 and stoichiometric Pb-terminated PTO[11]. SO_2 interacts with the surface with positive polarization vigorously. The binding energy is much smaller for different adsorption configurations in the case of paraelectricity. On the surface with negative polarization, SO_2 takes one of the surface oxygens away to form SO_3. Therefore, it would be more appropriate by describing this configuration as an SO_3 molecule on a surface with an oxygen vacancy. The calculated binding energy as negative and small implies that SO_3 is easily desorbed. Therefore, the negative polarization of random PTO exposed to SO_2 molecules may boost the formation of SO_3[11].

NO_x direct decomposition on PTO: Kakekhani *et al.*[11] reported that at reasonably low coverage (≤ 0.25 ML), both NO and NO_2 favor the dissociation and formation of bound N and O on the surface of the positively polarized PTO. Two such N atoms couple to create N_2 molecules, which are weakly bonded and desorb from the surface, yet the surface is poisoned by the powerfully bonded O atoms. Cleaning the poisoned surface with modifying the polarization to paraelectric or negative is recommended. Through this approach, the oxygen adsorption becomes weaker to form an O_2 molecule, which then leaves the surface. Once being cleaned, by bringing the surface back to positive polarization, the surface can be prepared for the next cycle. Based on the finding, it is possible to perform the entire decomposition reaction of $2NO_2 \rightarrow N_2 + 2O_2$ or $2NO \rightarrow N_2 + O_2$ by addressing the positive polarization for the reduction part of the reaction (NO/NO_2 reduction) and the negative/paraelectric for the oxidation part (O + O $\rightarrow O_2$)[11].

FUTURE CHALLENGES

Even polarization has shown a significant impact on catalytic performance and is regarded as the promising approach to boost activity and efficiency. However, there remain many unsolved problems and challenges, which require urgent and comprehensive investigations in the near future. Several possible research directions are listed and discussed below.

Ultrafast reversal of polarization
According to the conventional transition state theory[101-103], the reaction time τ for one step in a redox reaction can be roughly expressed as:

$$\tau = \omega^{-1} \exp(\frac{E^*}{K_B T})$$

where T, K_B, E^* and ω are the reaction temperature, Boltzmann constant, energy barrier and attempt frequency, respectively. For an ideal reaction, the reaction temperature is room temperature (300 K) and the energy barrier is less than 0.1 eV. The ω is selected to be 10^{13} s^{-1}[104,105]. Hence, the reaction time is on the picosecond time scale. To use polarization reversal to accelerate a reaction, the speed of this reversal process needs to be ultrafast, faster than the ideal reaction speed at least. However, the polarization reversal duration via the usual static or pulsed electric fields is around hundreds of picoseconds[106]. There have been some suggestions to toggle the polarization on the picosecond time scale through direct excitation of the ferroelectric mode using ultrashort radiation pulses[107-109] or stimulation of the electronic subsystem by light pulses[110]. The frequency adjustable range of high-intensity far-infrared electromagnetic field sources is too low. Nevertheless, these effects are by no means so high as to permit switching of the polarization via resonant pumping of the ferroelectric pattern. Recently, Abalmasov[111] proposed that the polarization can be ultimately reversed by a mid-infrared pulse if the depolarizing field is shielded, as in the case of a crystalline top metal wire around the pump laser spot (see Figure 5A). More effective theoretical and experimental strategies are still needed to achieve the ultrafast reversal of polarization.

Magnetic field control of chemical reactions through magnetoelectric effect
Recently, the magnetic reinforcement of electrocatalytic OER has been reported[112,113], namely, where an external magnetic field can improve the OER catalytic efficiency, because it strengths the adsorption of oxygen intermediates and electron transfer by enhancing the spin polarization of the catalysts. Furthermore, it has been reported that, as shown in Figure 5B, the magnetic field may also alter the polarization of the polarized surface in response to strain, an effect termed strain-mediated magnetoelectricity[114,115]. Revised polarization states can be believed to lead to reactive modulation. Therefore, a strain-mediated magnetoelectric effect in a magnetoelectric sample enables magnetic field control of chemical reactions at the polarized surface[115]. For some multiferroic materials (coexistence of ferromagnetism and ferroelectricity), both their spin and electric polarizations can be tuned by an external magnetic field. The magnetic reinforcement for electrocatalytic reactions may be more obvious, which needs further theoretical and experimental verification at a later stage.

In-plane polarization
Until now, most studies of polarization-driven catalysis have focused on tunable polarization with a direction perpendicular to the surface. In this case, the depolarization field usually causes electronic and atomic reconstruction simultaneously, which change the surface chemistry in complicated ways. Thus, the fundamental nature of the chemical properties associated with polarization is still far from being fully understood. In contrast, the depolarization fields will be absent for the system with in-plane polarization. The chemical properties of the polarized surface can be reflected more intrinsically by the interaction of in-plane polarization and surface adsorption[116], which may be an important area of interest in this field in the future.

Transport polarization
In an electrocatalytic reaction, the electron exchange between the substrate and the loaded catalyst is a key electron-dependent step. In addition to the redistribution of electrons necessitated by balanced chemical potential, the electron exchange also involves the flow of electrons across the interface at an overpotential, i.e., the injection of non-equilibrium electrons under an applied bias. Recently, by means of pulse voltammetry and X-ray absorption spectroscopy experiments, Nong *et al.*[117] discovered the influence of non-equilibrium carriers on electrocatalytic activity. On the basis of the electron transport state of a Ni cluster/graphene, Bian *et al.*[118] revealed that high spin polarization can result in electronic self-excitation effects, which induced the increased electronic system energy, enhanced reduction reaction thermodynamics and facilitated catalytic activity. Research on the electron state changes in the process of
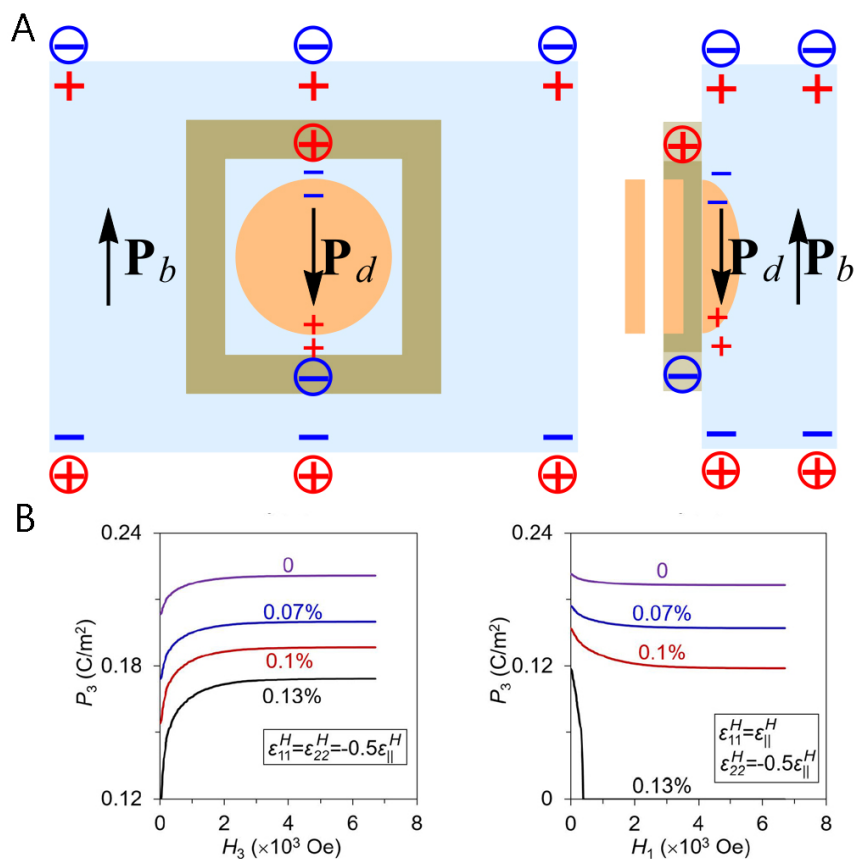
Figure 5. (A) Schematic of the screen surrounding the pump laser spot with the top of the crystal (gold color) and a sketch of the charge distribution (the free charge is enclosed within the circle)[111]. (B) The out-of-plane polarization (P_3) of BTO (001) films is a reflection of the in-plane (H_1) and out-of-plane (H_3) magnetic field strength for different biaxially isotropic in-plane residual strains ε_0 (= ε_{11} = ε_{22})[115]. BTO: BaTiO$_3$.

electronic transport facilitates the comprehension of the high electrocatalytic reduction behavior of an iron series of electrodes. However, the absence of systematic comparison of thermodynamic and electronic structure factors makes it difficult to accurately assess the impact of transport polarization on electrocatalysis at present. In future catalyst design studies, transport polarizability needs to be regarded as an important performance descriptive factor.

CONCLUSION

In summary, we have reviewed the recent research achievements of polarization-dependent catalytic reactions. It has been found that for polarized catalysts, polarization orientation can adjust the reactivity and selectivity of various catalytic reactions by tuning miscellaneous fundamental properties, such as the electronic and adsorption performance. The effects of polarization on chemical reactivity have been demonstrated for water splitting, wastewater treatments, organic dye degradation, CO$_2$ reduction and redox reductions, implying the promising potential to utilize the polarization to boost/optimize catalytic activity and surface chemistry. Even so, there remain many challenges to utilizing polarization in practical catalytic applications, as summarized/discussed at the end of this review.

DECLARATIONS

Authors' contributions
Literature search, and organization, manuscript drafting: Ju L, Tang X
Manuscript revision: Ju L, Tang X, Kou L
Project supervision: Ju L, Kou L

Conflicts of interest
All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate
Not applicable.

Consent for publication
Not applicable.

REFERENCES

1.   Wang Y, Skaanvik SA, Xiong X, Wang S, Dong M. Scanning probe microscopy for electrocatalysis. *Matter* 2021;4:3483-514. DOI
2.   Yue Q, Shao Z, Chang S, Li J. Adsorption of gas molecules on monolayer MoS_2 and effect of applied electric field. *Nanoscale Res Lett* 2013;8:425. DOI PubMed PMC
3.   Tang S, Cao Z. Adsorption of nitrogen oxides on graphene and graphene oxides: insights from density functional calculations. *J Chem Phys* 2011;134:044710. DOI PubMed
4.   Ao Z, Li S, Jiang Q. Correlation of the applied electrical field and CO adsorption/desorption behavior on Al-doped graphene. *Solid State Commun* 2010;150:680-3. DOI
5.   Park S, Lee CW, Kang MG, et al. A ferroelectric photocatalyst for enhancing hydrogen evolution: polarized particulate suspension. *Phys Chem Chem Phys* 2014;16:10408-13. DOI PubMed
6.   Garra J, Vohs J, Bonnell D. The effect of ferroelectric polarization on the interaction of water and methanol with the surface of $LiNbO_3(0001)$. *Surf Sci* 2009;603:1106-14. DOI
7.   Kakekhani A, Ismail-beigi S, Altman EI. Ferroelectrics: a pathway to switchable surface chemistry and catalysis. *Surf Sci* 2016;650:302-16. DOI
8.   Watanabe Y, Okano M, Masuda A. Surface conduction on insulating $BaTiO_3$ crystal suggesting an intrinsic surface electron layer. *Phys Rev Lett* 2001;86:332-5. DOI PubMed
9.   Yang W, Rodriguez BJ, Gruverman A, Nemanich RJ. Polarization-dependent electron affinity of $LiNbO_3$ surfaces. *Appl Phys Lett* 2004;85:2316-8. DOI
10. Sones CL, Mailis S, Brocklesby WS, Eason RW, Owen JR. Differential etch rates in z-cut $LiNbO_3$ for variable HF/HNO_3 concentrations. *J Mater Chem* 2002;12:295-8. DOI
11. Kakekhani A, Ismail-Beigi S. Polarization-driven catalysis via ferroelectric oxide surfaces. *Phys Chem Chem Phys* 2016;18:19676-95. DOI PubMed
12. Cui Y, Briscoe J, Dunn S. Effect of Ferroelectricity on solar-light-driven photocatalytic activity of $BaTiO_3$ - influence on the carrier separation and stern layer formation. *Chem Mater* 2013;25:4215-23. DOI
13. Li S, Bai L, Ji N, et al. Ferroelectric polarization and thin-layered structure synergistically promoting CO_2 photoreduction of Bi_2MoO_6. *J Mater Chem A* 2020;8:9268-77. DOI
14. Ju L, Tang X, Li J, Shi L, Yuan D. Breaking the out-of-plane symmetry of Janus WSSe bilayer with chalcogen substitution for enhanced photocatalytic overall water-splitting. *Appl Surf Sci* 2022;574:151692. DOI
15. Yuan Y, Reece TJ, Sharma P, et al. Efficiency enhancement in organic solar cells with ferroelectric polymers. *Nat Mater* 2011;10:296-302. DOI PubMed

16.   Garcia V, Bibes M, Bocher L, et al. Ferroelectric control of spin polarization. *Science* 2010;327:1106-10. DOI PubMed

17.   Morris MR, Pendlebury SR, Hong J, Dunn S, Durrant JR. Effect of internal electric fields on charge carrier dynamics in a ferroelectric material for solar energy conversion. *Adv Mater* 2016;28:7123-8. DOI PubMed

18.   Wu Q, Ma Y, Wang H, Zhang S, Huang B, Dai Y. Trifunctional electrocatalysts with high efficiency for the oxygen reduction reaction, oxygen evolution reaction, and Na-O_2 battery in heteroatom-doped Janus monolayer MoSSe. *ACS Appl Mater Interfaces* 2020;12:24066-73. DOI PubMed

19.   Kushwaha HS, Halder A, Vaish R. Ferroelectric electrocatalysts: a new class of materials for oxygen evolution reaction with synergistic effect of ferroelectric polarization. *J Mater Sci* 2018;53:1414-23. DOI

20.   Ju L, Bie M, Tang X, Shang J, Kou L. Janus WSSe monolayer: an excellent photocatalyst for overall water splitting. *ACS Appl Mater Interfaces* 2020;12:29335-43. DOI PubMed

21.   Shang J, Tang X, Kou L. Two dimensional ferroelectrics: candidate for controllable physical and chemical applications. *WIREs Comput Mol Sci* 2021:11. DOI

22.   Wan TL, Ge L, Pan Y, et al. Catalysis based on ferroelectrics: controllable chemical reaction with boosted efficiency. *Nanoscale* 2021;13:7096-107. DOI PubMed

23.   Abrahams SC, Nassau K. Ferroelectric materials. Concise encyclopedia of advanced ceramic materials. Elsevier; 1991. p. 152-5. DOI

24.   Su Y, Li Q, Amagat J, Chen M. 3D spring-based piezoelectric energy generator. *Nano Energy* 2021;90:106578. DOI

25.   Joshi JC, Dawar AL. Pyroelectric materials, their properties and applications. *phys stat sol (a)* 1982;70:353-69. DOI

26.   Xiao J, Zhu H, Wang Y, et al. Intrinsic two-dimensional ferroelectricity with dipole locking. *Phys Rev Lett* 2018;120:227601. DOI PubMed

27.   Cao Y, Li Q, Huijben M, Vasudevan RK, Kalinin SV, Maksymovych P. Electronic switching by metastable polarization states in $BiFeO_3$ thin films. *Phys Rev Materials* 2018;2:094401. DOI

28.   Yang X, Su X, Shen M, et al. Enhancement of photocurrent in ferroelectric films via the incorporation of narrow bandgap nanoparticles. *Adv Mater* 2012;24:1202-8. DOI PubMed

29.   Zubko P, Jung DJ, Scott JF. Electrical characterization of $PbZr_{0.4}Ti_{0.6}O_3$ capacitors. *J Appl Phys* 2006;100:114113. DOI

30.   Xue F, Liang L, Gu Y, Takeuchi I, Kalinin SV, Chen L. Composition- and pressure-induced ferroelectric to antiferroelectric phase transitions in Sm-doped $BiFeO_3$ system. *Appl Phys Lett* 2015;106:012903. DOI

31.   Park SM, Wang B, Das S, et al. Selective control of multiple ferroelectric switching pathways using a trailing flexoelectric field. *Nat Nanotechnol* 2018;13:366-70. DOI PubMed

32.   Zhang JX, Schlom DG, Chen LQ, Eom CB. Tuning the remanent polarization of epitaxial ferroelectric thin films with strain. *Appl Phys Lett* 2009;95:122904. DOI

33.   Li H, Sang Y, Chang S, et al. Enhanced ferroelectric-nanocrystal-based hybrid photocatalysis by ultrasonic-wave-generated piezophototronic effect. *Nano Lett* 2015;15:2372-9. DOI PubMed

34.   Akamatsu H, Yuan Y, Stoica VA, et al. Light-activated gigahertz ferroelectric domain dynamics. *Phys Rev Lett* 2018;120:096101. DOI PubMed

35.   Li T, Lipatov A, Lu H, et al. Optical control of polarization in ferroelectric heterostructures. *Nat Commun* 2018;9:3344. DOI PubMed PMC

36.   Sezen H, Suzer S. XPS for chemical- and charge-sensitive analyses. *Thin Solid Films* 2013;534:1-11. DOI

37.   Tănase LC, Apostol NG, Abramiuc LE, et al. Ferroelectric triggering of carbon monoxide adsorption on lead zirco-titanate (001) surfaces. *Sci Rep* 2016;6:35301. DOI PubMed PMC

38.   Pintilie L, Ghica C, Teodorescu CM, et al. Polarization induced self-doping in epitaxial $Pb(Zr_{0.20}Ti_{0.80})O_3$ thin films. *Sci Rep* 2015;5:14974. DOI PubMed PMC

39.   Apostol NG, Stoflea LE, Lungu GA, et al. Band bending at free $Pb(Zr,Ti)O_3$ surfaces analyzed by X-ray photoelectron spectroscopy. *Mater Sci Eng B* 2013;178:1317-22. DOI

40.   Popescu DG, Huşanu MA, Trupina Combining Caron L, et al. Spectro-microscopic photoemission evidence of charge uncompensated areas in $Pb(Zr,Ti)O_3(001)$ layers. *Phys Chem Chem Phys* 2015;17:509-20. DOI PubMed

41.   Abramiuc LE, Tănase LC, Barinov A, et al. Polarization landscape effects in soft X-ray-induced surface chemical decomposition of lead zirco-titanate, evidenced by photoelectron spectromicroscopy. *Nanoscale* 2017;9:11055-67. DOI PubMed

42.   Huşanu MA, Popescu DG, Tache CA, et al. Photoelectron spectroscopy and spectro-microscopy of $Pb(Zr,Ti)O_3$ (111) thin layers: Imaging ferroelectric domains with binding energy contrast. *Appl Surf Sci* 2015;352:73-81. DOI

43.   Tian Y, Wei L, Zhang Q, et al. Water printing of ferroelectric polarization. *Nat Commun* 2018;9:3809. DOI PubMed PMC

44.   Wang RV, Fong DD, Jiang F, et al. Reversible chemical switching of a ferroelectric film. *Phys Rev Lett* 2009;102:047601. DOI PubMed

45.   Highland MJ, Fister TT, Fong DD, et al. Equilibrium polarization of ultrathin $PbTiO_3$ with surface compensation controlled by oxygen partial pressure. *Phys Rev Lett* 2011;107:187602. DOI PubMed

46.   Highland MJ, Fister TT, Richard MI, et al. Polarization switching without domain formation at the intrinsic coercive field in ultrathin ferroelectric $PbTiO_3$. *Phys Rev Lett* 2010;105:167601. DOI

47.   Liu D, Zhao R, Jafri HM, Wang J, Huang H. Phase-field simulations of surface charge-induced polarization switching. *Appl Phys Lett* 2019;114:112903. DOI

48.   Deleuze P, Domenichini B, Dupont C. Ferroelectric polarization switching induced from water adsorption in $BaTiO_3$ ultrathin films. *Phys Rev B* 2020;101:075410. DOI

49.   Deleuze PM, Mahmoud A, Domenichini B, Dupont C. Theoretical investigation of the platinum substrate influence on $BaTiO_3$ thin film polarisation. *Phys Chem Chem Phys* 2019;21:4367-74. DOI PubMed

50.   Rodriguez BJ, Jesse S, Baddorf AP, Kim SH, Kalinin SV. Controlling polarization dynamics in a liquid environment: from localized to macroscopic switching in ferroelectrics. *Phys Rev Lett* 2007;98:247603. DOI PubMed

51.   Sobhan M, Xu Q, Yang Q, Anariba F, Wu P. Tunable atomic termination in nano-necklace $BiFeO_3$. *Appl Phys Lett* 2014;104:051606. DOI

52.   Tănase LC, Abramiuc LE, Popescu DG, et al. Polarization orientation in lead zirconate titanate (001) thin films driven by the interface with the substrate. *Phys Rev Applied* 2018;10:034020. DOI

53.   Pintilie I, Trinca L, Trupina L, Pasuk I, Pintilie L. Relation between domain structure and pyroelectric response in as-grown epitaxial $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films on substrates with different resistivity. *Mater Res Bull* 2017;93:201-7. DOI

54.   Ju L, Bie M, Shang J, Tang X, Kou L. Janus transition metal dichalcogenides: a superior platform for photocatalytic water splitting. *J Phys Mater* 2020;3:022004. DOI

55.   Ju L, Liu P, Yang Y, Shi L, Yang G, Sun L. Tuning the photocatalytic water-splitting performance with the adjustment of diameter in an armchair WSSe nanotube. *J Energ Chem* 2021;61:228-35. DOI

56.   Kakekhani A, Ismail-beigi S. Ferroelectric-based catalysis: switchable surface chemistry. *ACS Catal* 2015;5:4537-45. DOI

57.   Kakekhani A, Ismail-beigi S. Ferroelectric oxide surface chemistry: water splitting via pyroelectricity. *J Mater Chem A* 2016;4:5235-46. DOI

58.   Zhang Y, Kumar S, Marken F, et al. Pyro-electrolytic water splitting for hydrogen generation. *Nano Energy* 2019;58:183-91. DOI

59.   Xie M, Dunn S, Boulbar EL, Bowen CR. Pyroelectric energy harvesting for water splitting. *Int J Hydrogen Energy* 2017;42:23437-45. DOI

60.   You H, Jia Y, Wu Z, Wang F, Huang H, Wang Y. Room-temperature pyro-catalytic hydrogen generation of 2D few-layer black phosphorene under cold-hot alternation. *Nat Commun* 2018;9:2889. DOI PubMed PMC

61.   Xu X, Xiao L, Jia Y, et al. Pyro-catalytic hydrogen evolution by $Ba_{0.7}Sr_{0.3}TiO_3$ nanoparticles: harvesting cold-hot alternation energy near room-temperature. *Energy Environ Sci* 2018;11:2198-207. DOI

62.   Thuy Phuong PT, Zhang Y, Gathercole N, et al. Demonstration of enhanced piezo-catalysis for hydrogen generation and water treatment at the ferroelectric curie temperature. *iScience* 2020;23:101095. DOI PubMed PMC

63.   Kim HS. Computational design of a switchable heterostructure electrocatalyst based on a two-dimensional ferroelectric In_2Se_3 material for the hydrogen evolution reaction. *J Mater Chem A* 2021;9:11553-62. DOI

64.   Zhang L, Yang Z, Gong T, et al. Recent advances in emerging Janus two-dimensional materials: from fundamental physics to device applications. *J Mater Chem A* 2020;8:8813-30. DOI

65.   Sante D, Stroppa A, Jain P, Picozzi S. Tuning the ferroelectric polarization in a multiferroic metal-organic framework. *J Am Chem Soc* 2013;135:18126-30. DOI

66.   Rinaldi C, Varotto S, Asa M, et al. Ferroelectric control of the spin texture in GeTe. *Nano Lett* 2018;18:2751-8. DOI PubMed PMC

67.   Stroppa A, Di Sante D, Barone P, et al. Tunable ferroelectric polarization and its interplay with spin-orbit coupling in tin iodide perovskites. *Nat Commun* 2014;5:5900. DOI PubMed

68.   Jain P, Stroppa A, Nabok D, et al. Switchable electric polarization and ferroelectric domains in a metal-organic-framework. *npj Quant Mater* 2016;1:16012. DOI

69.   Zhao P, Ma Y, Lv X, Li M, Huang B, Dai Y. Two-dimensional III2-VI3 materials: promising photocatalysts for overall water splitting under infrared light spectrum. *Nano Energy* 2018;51:533-8. DOI

70.   Li X, Li Z, Yang J. Proposed photosynthesis method for producing hydrogen from dissociated water molecules using incident near-infrared light. *Phys Rev Lett* 2014;112:018301. DOI PubMed

71.   Ju L, Shang J, Tang X, Kou L. Tunable photocatalytic water splitting by the ferroelectric switch in a 2D $AgBiP_2Se_6$ monolayer. *J Am Chem Soc* 2020;142:1492-500. DOI PubMed

72.   Ortiz N, Zoellner B, Kumar V, et al. Composite ferroelectric and plasmonic particles for hot charge separation and photocatalytic hydrogen gas production. *ACS Appl Energy Mater* 2018;1:4606-16. DOI

73.   Gao Y, de Jubera AMS, Mariñas BJ, Moore JS. Nanofiltration membranes with modified active layer using aromatic polyamide dendrimers. *Adv Funct Mater* 2013;23:598-607. DOI

74.   Wu C, Zhang S, Yang D, Jian X. Preparation, characterization and application of a novel thermal stable composite nanofiltration membrane. *J Membrane Sci* 2009;326:429-34. DOI

75.   Pu L, Xu Y, Xia Q, et al. Ferroelectric membrane for water purification with arsenic as model pollutant. *Chem Eng J* 2021;403:126426. DOI

76.   Pan M, Liu S, Chew JW. Unlocking the high redox activity of MoS_2 on dual-doped graphene as a superior piezocatalyst. *Nano Energy* 2020;68:104366. DOI

77.   Chang J, Lin H. Exploitation of piezoelectricity for enhancing photocatalytic activity of ZnO nanowires. *Mater Lett* 2014;132:134-7. DOI

78.   Feng Y, Ling L, Wang Y, et al. Engineering spherical lead zirconate titanate to explore the essence of piezo-catalysis. *Nano Energy* 2017;40:481-6. DOI

79.   Lin J, Tsao Y, Wu M, Chou T, Lin Z, Wu JM. Single- and few-layers MoS_2 nanocomposite as piezo-catalyst in dark and self-powered active sensor. *Nano Energy* 2017;31:575-81. DOI

80.   Wu J, Qin N, Bao D. Effective enhancement of piezocatalytic activity of $BaTiO_3$ nanowires under ultrasonic vibration. *Nano Energy* 2018;45:44-51. DOI

81. Singh S, Khare N. Coupling of piezoelectric, semiconducting and photoexcitation properties in $NaNbO_3$ nanostructures for controlling electrical transport: realizing an efficient piezo-photoanode and piezo-photocatalyst. *Nano Energy* 2017;38:335-41. DOI

82. Liu X, Xiao L, Zhang Y, Sun H. Significantly enhanced piezo-photocatalytic capability in $BaTiO_3$ nanowires for degrading organic dye. *J Materiomics* 2020;6:256-62. DOI

83. Zhang Z, Zou C, Yang S, Yang Z, Yang Y. Ferroelectric polarization effect promoting the bulk charge separation for enhance the efficiency of photocatalytic degradation. *Chem Eng J* 2021;410:128430. DOI

84. Fu Q, Wang X, Li C, et al. Enhanced photocatalytic activity on polarized ferroelectric $KNbO_3$. *RSC Adv* 2016;6:108883-7. DOI

85. Chen Y, Li CW, Kanan MW. Aqueous CO_2 reduction at very low overpotential on oxide-derived Au nanoparticles. *J Am Chem Soc* 2012;134:19969-72. DOI PubMed

86. Kuhl KP, Hatsukade T, Cave ER, Abram DN, Kibsgaard J, Jaramillo TF. Electrocatalytic conversion of carbon dioxide to methane and methanol on transition metal surfaces. *J Am Chem Soc* 2014;136:14107-13. DOI PubMed

87. Savéant JM. Molecular catalysis of electrochemical reactions. Mechanistic aspects. *Chem Rev* 2008;108:2348-78. DOI PubMed

88. Kondratenko EV, Mul G, Baltrusaitis J, Larrazábal GO, Pérez-ramírez J. Status and perspectives of CO_2 conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes. *Energy Environ Sci* 2013;6:3112. DOI

89. Qiao J, Liu Y, Hong F, Zhang J. A review of catalysts for the electroreduction of carbon dioxide to produce low-carbon fuels. *Chem Soc Rev* 2014;43:631-75. DOI PubMed

90. Olah GA, Prakash GK, Goeppert A. Anthropogenic chemical carbon cycle for a sustainable future. *J Am Chem Soc* 2011;133:12881-98. DOI PubMed

91. Han N, Wang Y, Yang H, et al. Ultrathin bismuth nanosheets from in situ topotactic transformation for selective electrocatalytic CO_2 reduction to formate. *Nat Commun* 2018;9:1320. DOI PubMed PMC

92. Zhang Y, Zhang X, Ling Y, Li F, Bond AM, Zhang J. Controllable synthesis of few-layer bismuth subcarbonate by electrochemical exfoliation for enhanced CO_2 reduction performance. *Angew Chem Int Ed Engl* 2018;57:13283-7. DOI PubMed

93. Li F, Chen L, Knowles GP, MacFarlane DR, Zhang J. Hierarchical mesoporous SnO_2 nanosheets on carbon cloth: a robust and flexible electrocatalyst for CO_2 reduction with high efficiency and selectivity. *Angew Chem Int Ed Engl* 2017;56:505-9. DOI PubMed

94. Guo SX, Li F, Chen L, MacFarlane DR, Zhang J. Polyoxometalate-promoted electrocatalytic CO_2 reduction at nanostructured silver in dimethylformamide. *ACS Appl Mater Interfaces* 2018;10:12690-7. DOI PubMed

95. Wang H, Jia J, Song P, et al. Efficient electrocatalytic reduction of CO_2 by nitrogen-doped nanoporous carbon/carbon nanotube membranes: a step towards the electrochemical CO_2 refinery. *Angew Chem Int Ed Engl* 2017;56:7847-52. DOI PubMed

96. Lin S, Diercks CS, Zhang YB, et al. Covalent organic frameworks comprising cobalt porphyrins for catalytic CO_2 reduction in water. *Science* 2015;349:1208-13. DOI PubMed

97. Zhang X, Sun X, Guo S, Bond AM, Zhang J. Formation of lattice-dislocated bismuth nanowires on copper foam for enhanced electrocatalytic CO_2 reduction at low overpotential. *Energy Environ Sci* 2019;12:1334-40. DOI

98. Lee SY, Jung H, Kim NK, Oh HS, Min BK, Hwang YJ. Mixed copper states in anodized Cu electrocatalyst for stable and selective ethylene production from CO_2 reduction. *J Am Chem Soc* 2018;140:8681-9. DOI PubMed

99. Ju L, Tan X, Mao X, et al. Controllable CO_2 electrocatalytic reduction via ferroelectric switching on single atom anchored In_2Se_3 monolayer. *Nat Commun* 2021;12:5128. DOI PubMed PMC

100. Song W, Salvador PA, Rohrer GS. Influence of the magnitude of ferroelectric domain polarization on the photochemical reactivity of $BaTiO_3$. *ACS Appl Mater Interfaces* 2018;10:41450-7. DOI PubMed

101. Beheshtian J, Peyghan AA, Noei M. Sensing behavior of Al and Si doped BC_3 graphenes to formaldehyde. *Sensor Actuat B-Chem* 2013;181:829-34. DOI

102. Zhang YH, Chen YB, Zhou KG, et al. Improving gas sensing properties of graphene by introducing dopants and defects: a first-principles study. *Nanotechnology* 2009;20:185504. DOI PubMed

103. Ma D, Ju W, Li T, et al. Formaldehyde molecule adsorption on the doped monolayer MoS_2: a first-principles study. *Appl Surf Sci* 2016;371:180-8. DOI

104. Weigelt S, Busse C, Bombis C, et al. Covalent interlinking of an aldehyde and an amine on a Au(111) surface in ultrahigh vacuum. *Angew Chem* 2007;119:9387-90. DOI PubMed

105. Kokalj A. Formation and structure of inhibitive molecular film of imidazole on iron surface. *Corros Sci* 2013;68:195-203. DOI

106. Li J, Nagaraj B, Liang H, Cao W, Lee CH, Ramesh R. Ultrafast polarization switching in thin-film ferroelectrics. *Appl Phys Lett* 2004;84:1174-6. DOI

107. Fahy S, Merlin R. Reversal of ferroelectric domains by ultrashort optical pulses. *Phys Rev Lett* 1994;73:1122-5. DOI PubMed

108. Herchig R, Chang C, Mani BK, Ponomareva I. An unusual route to polarization reversal in ferroelectric ultrathin nanowires. *Appl Phys Lett* 2014;105:012907. DOI

109. Qi T, Shin YH, Yeh KL, Nelson KA, Rappe AM. Collective coherent control: synchronization of polarization in ferroelectric $PbTiO_3$ by shaped THz fields. *Phys Rev Lett* 2009;102:247603. DOI PubMed

110. Lian C, Ali ZA, Kwon H, Wong BM. Indirect but efficient: laser-excited electrons can drive ultrafast polarization switching in ferroelectric materials. *J Phys Chem Lett* 2019;10:3402-7. DOI PubMed

111. Abalmasov VA. Ultrafast reversal of the ferroelectric polarization by a midinfrared pulse. *Phys Rev B* 2020;101:014102. DOI

112. Ren X, Wu T, Sun Y, et al. Spin-polarized oxygen evolution reaction under magnetic field. *Nat Commun* 2021;12:2608. DOI PubMed PMC

113. Yan J, Wang Y, Zhang Y, Xia S, Yu J, Ding B. Direct magnetic reinforcement of electrocatalytic ORR/OER with electromagnetic

induction of magnetic catalysts. *Adv Mater* 2021;33:e2007525. DOI PubMed

114.   Hu JM, Chen LQ, Nan CW. Multiferroic heterostructures integrating ferroelectric and magnetic materials. *Adv Mater* 2016;28:15-39.
          DOI PubMed

115.   Hu J, Eom C. Magnetic-field control of ionic bonds on ferroelectric surfaces. *Appl Phys Lett* 2019;114:091601. DOI

116.   Wang ZW, Shu DJ. Intrinsic interaction between in-plane ferroelectric polarization and surface adsorption. *Phys Chem Chem Phys*
          2019;21:18680-5. DOI PubMed

117.   Nong HN, Falling LJ, Bergmann A, et al. Key role of chemistry versus bias in electrocatalytic oxygen evolution. *Nature*
          2020;587:408-13. DOI PubMed

118.   Bian F, Wu X, Li S, et al. Role of transport polarization in electrocatalysis: a case study of the Ni-cluster/Graphene interface. *J Mater
          Sci Technol* 2021;92:120-8. DOI