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Electrostatic-induced green and precise growth of model catalysts

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Crystallographic control of crystals as catalysts with precise geometrical and chemical features is significantly important to develop sustainable chemistry, yet highly challenging. Encouraged by first principles calculations, precise structure control of ionic crystals could be realized by introducing an interfacial electrostatic field. Herein, we report an efficient in situ dipole-sourced electrostatic field modulation strategy using polarized ferroelectret, for crystal facet engineering toward challenging catalysis reactions, which avoids undesired faradic reactions or insufficient field strength by conventional external electric field. Resultantly, a distinct structure evolution from tetrahedron to polyhedron with different dominated facets of Ag₃PO₄ model catalyst was obtained by tuning the polarization level, and similar oriented growth was also realized by ZnO system. Theoretical calculations and simulation reveal that the generated electrostatic field can effectively guide the migration and anchoring of Ag⁺ precursors and free Ag₃PO₄ nuclei, achieving oriented crystal growth by thermodynamic and kinetic balance. The faceted Ag₃PO₄ catalyst exhibits high performance in photocatalytic water oxidation and nitrogen fixation for valuable chemicals production, validating the effectiveness and potential of this crystal regulation strategy. Such an electrically tunable growth concept by electrostatic field provides new synthetic insights and great opportunity to effectively tailor the crystal structures for facet-dependent catalysis.

crystal facet engineering | interfacial electric field | dielectrophoretic force | facet-dependent catalysis | PVDF/PTFE ferroelectret

Sustainable chemistry such as (photo)catalysis using crystal catalysts, plays an ever-increasing important role for carbon neutral (1, 2). Crystallographic control of crystals with precise geometrical and chemical features provides great opportunity to modulate their physicochemical properties for optimizing relevant performance in challenging catalysis, where a high-energy crystal facet generally possesses even higher catalytic activity (3–7). Significant efforts through tuning the synthetic parameters and routes have been devoted to engineering specific morphology and crystal facets of catalysts for functional attributes over years (8–10). For example, many surfactants or capping agents have been employed to modulate the facet growth of crystals. However, these coordinated reagents would cap certain active sites on the surface, leading to considerable decay of facet-dependent reactivity (5, 9, 11). Moreover, the realization of complex crystal structures often undergoes complicated or multi-step reactions, resulting in limited synthetic universality and great difficulty for scale-up (12, 13). Therefore, developing facile and efficient synthetic strategies to tailor crystal structures for facet-dependent catalysis is highly desired.

Applying external stimuli such as electric field and magnetic field has been proven effective to control the crystal growth (9, 14, 15). According to the classical nucleation theory, electric field brings extra energy to the solution system that greatly changes the local chemical environment of ions and other electrically charged monomers (14), which could boost the nucleation and growth orientation (16–18). However, the undesired faradic reaction or limited field strength hinders the further development (19). Typically, the conventional (direct current) electric field applied usually acts in macroscale or mesoscale, while the realization of effective crystallization control in nanoscale requires a high field strength that reaches 10^5 V m⁻¹ or even higher, which is significantly difficult for nanosynthesis systems (14, 20). Electrostatic field, as an alternative source, can generate efficient local field strength (2). A recent study demonstrates that electrostatic field from ionic liquid can effectively guide local crystal rearrangement of porous organic cages (21).

Inspired by the prominent charge storage capability of ferroelectret, it is possible to in situ generate strong local electrostatic field for crystal growth (22–25). Typically, ferroelectret as a piezoelectrically active polymer with aligned domains yields a high permanent charge density to form space charge or dipole charge, thereby producing a local microscopic electrostatic field on its periphery (22, 23). Especially, the ferroelectric β -poly(vinylidene fluoride) (β -PVDF), with a maximum polarized charge density reaches

Significance

Typical structural engineering strategies for crystallographic control of catalysts generally require multi-step processes, including pre-/post-treatments, and/or surfactants, capping agents, which limit the fabrication flexibility. Applying external electric field with high convenience, efficiency and versatility, can simplify the process, while insufficient field strength or undesired faradic reactions hinder its further development. Herein, we report an impressive in situdipolesourced electrostatic field modulation strategy for crystal facet engineering of model catalyst, using Ag₃PO₄as a proof of concept. Such a dipolesourced and electrically tunable strategy substantially shortens synthetic steps and avoids the surfactants or capping agents that may alter the catalytic reactivity. This methodology brings more possibilities for engineering crystal structures for sustainable chemistry.

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0.12 cm⁻² (-0.75 e nm⁻²) (26), could be served as an ideal micro-electric field source with calculated field strength up to 10^7 V m⁻¹ magnitude (COMSOL simulation), which is much higher than that of common materials [e.g., polypropylene or polyacry-lonitrile (PAN)] (27, 28). Ag₃PO₄ ionic semiconductor with multiple advantages such as applicable bandgap for visible light response, low toxicity, high quantum efficiency up to 90% and high catalytic activity especially on (111) facet (29, 30), is selected as a proof-of-concept model crystal catalyst to verify the feasibility of above hypothesis.

For the first time, to our best knowledge, we propose an efficient in situ dipole-sourced interfacial electrostatic field modulation strategy using ferroelectret, for precise growth control of model crystal catalysts with oriented morphology and facet features. By varying the strength of ferroelectric polarization, a notable faceted structure evolution of Ag₃PO₄ crystals was obtained. Theoretical calculations and COMSOL simulation further suggested a possible growth protocol between the tunable crystal structures and dipole-sourced electrostatic field on ferroelectret. The generated electrostatic field facilitates the capture of Ag⁺ onto ferroelectret substrate under electrostatic force and guides the migration of free nuclei toward ferroelectret by dielectrophoretic force from the non-uniform interfacial electrostatic field, where the two determine the oriented growth of Ag₃PO₄ crystals upon different field strength by kinetic control. The rationally designed faceted catalysts exhibited high efficiencies toward photocatalytic water splitting and nitrogen fixation for valuable chemicals production, validating the effectiveness and application potential of this crystal regulation strategy. The effectiveness and universality of this synthetic methodology were further verified by the oriented growth of ZnO crystals. Such an electrically tunable strategy by ferroelectret-induced electrostatic field substantially simplifies synthetic steps, avoids capping agents, and broadens the synthetic scopes for oriented crystals.

Results and Discussion

Dipole-Sourced Interfacial Electric Field on Ferroelectret. PVDF/PTFE ferroelectret nanofibers (NFs) were produced by one-step additive-assisted electrospinning approach, which can achieve in situ charging of electret during the formation of fibers induced by the high strength of electric field applied and the stretching of shear field (Fig. 1A) (31, 32). PTFE nanoparticles (SI Appendix, Fig. S1), served as a local strong charge enhancer (26, 33–35), were added to generate stable dipole charges with the polarized β -phase PVDF domains (23), forming a radial interfacial electrical field on the fiber surface with spatial gradient distribution. Herein, three ferroelectret samples with different polarization levels, i.e., different polar β-PVDF contents, were prepared to study the influence of field strength on grown crystal structures, under the synergistic effect of varying solvent ratio and working voltage, denoted as PVDF/PTFE_{low}, PVDF/PTFE_{mid} and PVDF/PTFE_{high} NFs, respectively. The obtained PVDF/PTFE NFs possess an average diameter of 200 ~ 400 nm without notable surface roughness (Fig. 1 B and C and SI Appendix, Fig. S2).

To directly visualize the ferroelectric polarization distribution, Kelvin probe force microscopy (KPFM) measurements were performed on a single NF. As shown in Fig. 1*B*, the KPFM potential image exhibits a relatively homogeneous surface potential of -0.7V along the axial direction of PVDF/PTFE_{low} fiber, enabling a radial interfacial electrostatic field with gradient distribution. Similar KPFM potential distribution was also observed in PVDF/ PTFE NFs with higher polarization but more negative potential values (Fig. 1*C* and *SI Appendix*, Fig. S2*A*), suggesting higher electric field strength. For fair comparison, electrospun NFs of non-ferroelectret polyacrylonitrile (PAN) were fabricated. Notably, electric potential values of PVDF/PTFE ferroelectret NFs are three orders of magnitude higher than PAN NFs (*SI Appendix*, Fig. S3, in mV level), which could generate a variable electric field with strength up to magnitude of 10^7 V m⁻¹ enabling further crystal growth manipulation (COMSOL simulation part).

Consistent with the evolution of electrostatic potential by different ferroelectric polarization, PVDF/PTFE_{high} NFs show the highest β -phase crystallinity of 88.6%, which is much higher than that of PVDF/PTFE_{low} NFs (69.7%), determined by Fourier transform infrared spectroscopy (FT-IR, Fig. 1D) and X-ray diffraction (XRD, SI Appendix, Fig. S4) measurements (26, 36). Typically, the oriented ferroelectric domains of β -PVDF could introduce strong dipolar charges, contributing to electret-based transduction with improved electrical capacity (35). Zeta potential results also confirm more negative potential of PVDF/PTFE NFs with higher polarization level (SI Appendix, Fig. S5). Moreover, as shown in Fig. 1E, piezoresponse force microscopy (PFM) analysis demonstrates a distinct ferroelectricity property of PVDF/ PTFE NFs, which yields a permanent polarization with oriented electric domains for storing abundant charges (37). These results suggest that the obtained PVDF/PTFE ferroelectret NFs with notable ferroelectric features are a promising and tunable micro-electric field source, which is expected to effectively modulate the crystal growth of catalysts.

Engineering Crystal Facet and Morphology of Ag₃PO₄ Crystals. Investigation of the crystal facet and morphology control of Ag₃PO₄ crystals was conducted via an in situ growth approach under the ferroelectret-induced interfacial electrostatic field (Fig. 2A). Fig. 2 B-D shows the structure and morphology variation of Ag₃PO₄ crystals grown on as-prepared ferroelectret NFs. Typically, bare Ag₃PO₄ crystals grown without substrate, display an irregular (sub)micrometer-sized particle morphology without preferential specific facet exposed (Fig. 2B). Interestingly, by introducing PVDF/PTFE ferroelectret NFs at a relatively low polarization level, Ag₃PO₄ crystals appear to form regular tetrahedron structure with a particle size of -3 to 5 μm grown on the fibers, forming a necklace-like PVDF/PTFE@Ag₃PO₄ heterostructure (Fig. 2C and *SI Appendix*, Fig. S6A). Certainly, the crystal size could be well tuned by controlling the growth duration (SI Appendix, Fig. S7). Strikingly, using PVDF/PTFE_{high} NFs, the morphology of Ag₃PO₄ crystal turns from tetrahedron to polyhedron with slightly reduced particle size (Fig. 2D and *SI Appendix*, Fig. S6B). Obviously, as shown in SI Appendix, Fig. S8A, the intermediate PVDF/PTFE_{mid}@Ag₃PO₄ heterostructure exhibits a transition state morphology, confirming the above crystal growth hypothesis. Meanwhile, SEM energy-dispersive spectroscopy (EDS) elemental maps (*SI Appendix*, Fig. S9A) show a uniform spatial distribution of Ag, P, and O elements in the grown tetrahedrons, ensuring homogeneous catalytic activity. Ag₃PO₄ crystals were also produced using the non-ferroelectret PAN NFs, in which no distinct crystal facet control was observed (*SI Appendix*, Fig. S10). Briefly, the typical structure evolution of in situ grown Ag_3PO_4 crystals well corresponds to the polarization potential variation of PVDF/PTFE ferroelectret NFs.

Transmission electron microscopy (TEM) images were taken to study the structure and facet evolution of as-grown Ag_3PO_4 crystals. As shown in *SI Appendix*, Figs. S9 and S11, Ag_3PO_4 crystals show typical tetrahedron and polyhedron morphology. Selected area electron diffraction (SAED) patterns of Ag_3PO_4 crystals reveal that tetrahedron displays (110), (011) facets, polyhedron exposes facets containing (110) and (002) facets, and



Fig. 1. Fabrication of PVDF/PTFE ferroelectret NFs. (*A*) Schematic showing the dipole polarization and orientation of PVDF/PTFE NFs during the electrospinning process. (*B* and *C*) SEM, AFM height, and corresponding KPFM potential map images of PVDF/PTFE NFs. All bars are the same correspondingly. (*D*) FT-IR spectra of the PVDF powder and PVDF/PTFE NFs. *Inset* is the β -phase content, F(β) value. (*E*) Amplitude butterfly curve and phase hysteresis loop of PVDF/PTFE Image. NFs.

irregular Ag₃PO₄ crystals show mixed facets features, respectively (12, 38, 39). To further confirm the Ag₃PO₄ crystal facet exposed, XRD measurements were carried out on the obtained heterostructures. As shown in Figs. 2*E* and *SI Appendix*, Fig. S8*B*, all the samples display the characteristic peaks corresponding to crystal-line cubic Ag₃PO₄ (JCPDS 06-0505). As reported in many studies (12, 39, 40), the main peak intensity ratios of (110)/(200) and (222)/(200) were calculated to estimate the dominated facets of Ag₃PO₄ crystals. Obvious variation in the peak intensity ratios is observed (Fig. 2*E*), which firmly supports the above structure evolution results. Specifically, Ag₃PO₄ tetrahedrons grown on PVDF/PTFE_{low} NFs present a highest (222)/(200) intensity ratio of 1.36, indicating that tetrahedrons primarily expose (111) facets. By contrast, polyhedrons with multifacets exhibit more (110)

facets due to its highest intensity ratio of (110)/(200) (12, 30, 40). The morphology and facet control of growing Ag₃PO₄ crystals demonstrates that such an electrostatic-involved growth approach is facile and effective, free of capping agents or multi-step control (30, 41).

Theoretical Understanding of Electrostatic Field-modulated Crystal Growth. The above observations have demonstrated effective structure and facet manipulation of Ag_3PO_4 crystals by engineering ferroelectret substrate, while the growth mechanism remains unclear. Generally, applying external electric field can regulate the nucleation and growth of materials, especially starting from electrically charged monomers or ionic precursors (9, 14). Herein, ferroelectret PVDF/PTFE NFs with dipole



Fig. 2. Structure and morphology evolution of Ag_3PO_4 crystals grown on PVDF/PTFE NFs. (*A*) Schematic showing the growth of faceted Ag_3PO_4 crystals under the ferroelectret-induced interfacial electrostatic field. Where F_e represents electric field force including electrostatic and F_{dep} is dielectrophoretic force for trapping ions and nuclei, and E_{int} is interfacial electric field. Typical SEM images of relevant Ag_3PO_4 crystals are provided. (Scale bar: 1 µm.) (*B–D*) Representative SEM images of pure Ag_3PO_4 , PVDF/PTFE_{low}@Ag_3PO_4(111) and PVDF/PTFE_{high}@Ag_3PO_4. (*E*) XRD patterns of Ag_3PO_4 crystals. *Inset* showing the crystal structure and peak intensity ratios of (222)/(200) and (110)/(200) for Ag_3PO_4 crystals.

charges generated were employed as a micro-electrostatic field source (perpendicularly to fiber), which is expected to control the nucleation and growth processes of Ag₃PO₄ crystals. First principles calculations were performed to thermodynamically understand the growth behaviors. To simplify the calculation model, density functional theory (DFT) calculations were carried out on the preference adsorption between Ag⁺ (or faceted Ag₃PO₄) and $\alpha(\beta)$ -PVDF substrate, in that polar β -PVDF affords the ferroelectric property to generate electrostatic field. Optimized structures of Ag⁺ adsorbed on armchair-edged nonpolar α-PVDF and zigzagedged polar β -PVDF were established (*SI Appendix*, Fig. S12). As shown in Fig. 3 A and B, the results suggest that Ag^+ tends to adsorb on F-side of β -PVDF instead of α -PVDF, determined by the more negative adsorption energy (E_{ads} , -2.35 eV on β -PVDF, -1.26 eV on α -PVDF). Calculation on partially polarized PVDF (50% β -PVDF by replacing F with H) was conducted to simulate practical conditions, which also shows more negative E_{ads} of -2.10 eV than α -PVDF to capture Ag⁺ (Fig. 3*C*). *SI Appendix*, Fig. S13 shows the results of Ag⁺ adsorption by the ferroelectret substrate, where the PVDF/PTFE ferroelectret with a higher polarization level delivered a higher Ag⁺ capture capacity, firmly supporting the calculations as expected.

To further understand the Ag⁺ adsorption on β -PVDF, adsorption-induced charge difference was investigated on both F- and H-side of β -PVDF. As shown in Fig. 3 *D* and *E*, there is a significant difference in charge transfer when Ag⁺ adsorbed on the two sides of β -PVDF. Charge dissipation (accumulation) mainly occurs near the interface of Ag⁺ on the F-side (or H-side) of β -PVDF. Moreover,

the interfacial charge redistribution is more intense when Ag⁺ adsorbed on the F-side of β -PVDF compared with H-side. Fig. 3 *F* and *G* shows the electrostatic potential (*V*) of Ag⁺/F-side β -PVDF, Ag⁺/H-side β -PVDF, where the gray line represents the *V* of β -PVDF. The charge polarization is aggravated at the Ag⁺/ β -PVDF interface, indicating the formation of an interfacial dipole, accompanied by a potential step (ΔV_1). In accordance with hypothesis, β -PVDF affords an intrinsic dipole, evidenced by the large potential difference between the top and the bottom sides ($\Delta V_2 = 3.96 \text{ eV}$). The decreased magnitude of interfacial dipole (ΔV) for Ag⁺/ β -PVDF is originating from the opposite direction of dipole generated on interface and intrinsic dipole of β -PVDF. The much larger ΔV demonstrates much higher adsorption strength of Ag⁺ on the F-side (0.69 eV) of β -PVDF than the H-side (0.18 eV).

Above results demonstrate the adsorption priority of Ag^+ precursor on F-side of β -PVDF for nucleation, where heterogeneous nucleation of Ag_3PO_4 on PVDF substrate is favorable due to the lowered energy barrier compared with homogeneous nucleation (9, 42–44). To figure out the faceted growth of Ag_3PO_4 crystals, adsorption of an individual $\alpha(\beta)$ -PVDF chain onto different crystal facets of Ag_3PO_4 including (111) and (110), was calculated. As shown in Fig. 3 *H*–*K*, similar to the adsorption of Ag^+ on PVDF, β -PVDF adsorbs more strongly on the Ag_3PO_4 by F-side than α -PVDF. Moreover, the adsorption of F-side β -PVDF on the (110) facet of Ag_3PO_4 was stronger than that on (111) facet, indicating that pure β -PVDF (strong electrostatic field) tends to adsorb on the Ag_3PO_4 (110), namely grown crystal with (110) facet exposed on ferroelectret with high polarization level. Considering that



Fig. 3. DFT calculations. (*A*-*C*) Most stable optimized structure (*Top* view and *Side* view) and corresponding adsorption energy (E_{ads}) of an individual Ag⁺ adsorbed on α-PVDF, β-PVDF, and 50% β-PVDF, respectively. (*D* and *E*) Plane-averaged charge difference ($\Delta \rho$) of Ag⁺ adsorbed on F- or H-side of β-PVDF along vertical z-direction to Ag⁺/β-PVDF interface, respectively. Virtualization background is the real-space charge difference of Ag⁺/β-PVDF, where yellow and blue regions represent charge accumulation and depletion, respectively. The isosurface level is set to be 0.0001 e Å⁻³. (*F* and *G*) Electrostatic potential (*V*) along Ag⁺/β-PVDF by F-side and H-side, respectively. The pink and gray lines represent the electrostatic potential of adsorption interface and pure β-PVDF. The vacuum level on the left was set to 0. (*H*-*K*) Optimized structure and corresponding E_{ads} of an individual α(β)-PVDF chain adsorbed on (110) or (111) facet of Ag₃-PO₄, respectively. *N_c* is the number of carbon atoms in PVDF. (*L*) Structure schemes of β-PVDF with different F atom ratios. (*M*) E_{ads} of β-PVDF with different F ratios on Ag₃-PO₄.

electrospun PVDF/PTFE fibers exhibit different crystallinity of β-PVDF (mixed α- and β-PVDF), different contents of β-PVDF by partially replacing F with H atoms for simulating the α/β heterojunction and simplifying the calculation model (Fig. 3*L*), were employed to study the adsorption on Ag₃PO₄ (111)/(110) and thereby projecting the growth orientation. The calculated results are summarized in Fig. 3*M* and *SI Appendix*, Table S1, where the adsorption strength of β-PVDF with lowered contents on Ag₃PO₄ (110) shows an overall decrease trend, while the variation of F ratio slightly alters the adsorption of β-PVDF on Ag₃PO₄ (111). The adsorption strength of β-PVDF at low contents on Ag₃PO₄ (111) is generally much higher than that on Ag₃PO₄ (110), suggesting that low-content β-PVDF (low electric field) facilitates the growth of Ag₃PO₄ with (111) facet exposed. Briefly, DFT calculations well support the experimental results.

COMSOL Simulation for understanding Dielectrophoresis Contribution. Generally, a dielectric particle (charged or neutral) located in an uneven electrical field will occur dielectrophoresis due to the induced dipole of particle and the field strength gradient (2, 45). Herein, the non-uniform interfacial electrostatic field provided by the polarized ferroelectret could contribute to dielectrophoresis regulation of free Ag₃PO₄ nuclei or tiny crystals

for crystal growth modulation. As schematically illustrated in Fig. 4A, typically, Ag⁺ precursors prefer to be trapped and adsorbed on the negatively charged F-rich fiber surface under the electrostatic field force, verified by DFT calculations, yielding heterogeneous nucleation and growth of Ag₃PO₄ after feeding with anion precursors (17, 46). Meanwhile, burst self-nucleation of Ag₃PO₄ often occurs under high precursor concentration. The ferroelectret NFs generate an uneven interfacial electrostatic field with radial gradient distribution, leading to dipolar polarization and possible migration of free Ag₃PO₄ nuclei in ethanol solution, which could be trapped by the ferroelectret NFs (high field strength on the surface) and grow to modulate the growth of Ag₃PO₄ crystals, socalled dielectrophoretic force (F_{DFP}) . To quantify the dielectrophoresis contribution, COMSOL Multiphysics simulation on tiny Ag₃PO₄ particles under ferroelectret-induced interfacial electrostatic field was performed. The F_{DEP} was calculated according to the following equation: (45)

$$F_{\text{DEP}} = 4\pi\varepsilon_0\varepsilon_r r_p^3 re[\tilde{K}](E\cdot\nabla)E$$

where $(E \cdot \nabla)E = \frac{1}{2}\nabla E^2$ represents the (geometric) gradient of the square of the field intensity E (V m⁻¹). Benefitting from the



Fig. 4. COMSOL simulation. (*A*) Schematic showing the nucleation and growth processes of Ag₃PO₄ crystals controlled by the ferroelectret-induced interfacial electrostatic field, where electrostatic and dielectrophoretic force act on ions and nuclei, respectively. (*B–D*) COMSOL simulation showing the induced electrostatic field, and *E–G*, dielectrophoretic force for trapping Ag₃PO₄ nuclei in 0.3 s simulation. A quarter of the fiber is selected to show dielectrophoretic enrichment. The white dots represent Ag₃PO₄ nuclei. All bars are the same correspondingly.

nanoscale diameter and high tortuous structure of NFs, the local periphery electric field strength was calculated up to 10^7 V m⁻¹ magnitude and extended for hundreds of nanometers (*SI Appendix, COMSOL Multiphysics Simulation*).

As shown in Fig. 4 *B* and *E*, since modicum adsorption of ions and nuclei is conducive for selective and kinetically oriented growth of crystals (9, 12, 14), the fewer and slower nuclei adhesion on $PVDF/PTFE_{low}$ NFs by the smaller F_{DEP} , allows growth of Ag₃PO₄ crystal in high-energy (111) facet with tetrahedron morphology. With increasing electric field strength by PVDF/PTFE_{high} NFs (Fig. 4 C and F), a much stronger F_{DEP} on free Ag₃PO₄ nuclei along with larger electrostatic force on Ag⁺ is presented. Notably, abundant nucleation and fast precursor capture along with free nuclei trapping would cause kinetic competition in Ag₃PO₄ growth on PVDF/ PTFE NFs, which tends to reduce the system Gibbs free energy by low-energy facet orientation to retain thermodynamic equilibrium (47). Consequently, Ag₃PO₄ polyhedrons with multifacets are obtained when employing highly polarized PVDF/PTFE_{high} NFs. Moreover, COMSOL simulation shows little nuclei trapped on the surface of PAN NFs (Fig. 4 D and G), supporting the growth result. Without dipole-sourced electrostatic field to provide electrostatic and dielectrophoretic force, free crystallization process leads to uncontrollable Ag_3PO_4 crystal growth outside the substrate.

To further verify this growth model, *operando* optical observation was carried out on planar optical growth system. As shown in *SI Appendix*, Fig. S14, *operando* visualization has clearly demonstrated the burst self-nucleation of Ag_3PO_4 outside the NFs and further anchoring onto the ferroelectret NFs, confirming the dielectrophoresis contribution of the interfacial electrostatic field. Overall, based on the experimental observation, theoretical calculations, and simulation, we have proposed a possible dipolesourced electrostatic-dependent growth model by the thermodynamic and kinetic balance, which obeys the classical nucleation theory framework, to explain the oriented growth behaviors of Ag_3PO_4 crystals on ferroelectret substrate.

Faceted Ag₃PO₄ Catalysts toward Water Splitting and Nitrogen Fixation. Generally, tuning the specific facets and morphology of crystal catalysts, i.e., the surface structures, can cause a dramatic change in fundamental properties to regulate the catalytic reactivity. Herein, the photocatalytic performance of faceted Ag₃PO₄ model catalyst was evaluated. As shown in Fig. 5, the electronic structures of as-prepared Ag_3PO_4 crystals were studied by the Tauc plot (48, 49), where a reasonably wide band gap of ~2.4 to 2.5 eV within the visible light spectrum is delivered. In particular, the $Ag_3PO_{4(111)}$ tetrahedron shows the highest band gap up to 2.51 eV and positive valence band reaching 2.72 eV among three samples (SI Appendix, Fig. S15), indicating the strongest holes (h^+) oxidation capabilities (12, 38). And a high-index facet with a higher surface energy is generally more reactive for catalysis reactions than the low-index one (4, 40). Therefore, the Ag₃PO₄ crystals were used as a potential photocatalyst toward challenging catalytic reactions involving water splitting or even nitrogen fixation (Fig. 5F). Ag₃PO₄ crystals were separated from the heterostructures to identify the facet role of Ag_3PO_4 in catalytic reactions.

Oxygen (O₂) evolution reaction (OER) was selected as a model reaction due to its high-value production of O₂, since it is more challenging because the formation of one molecular O₂ requires four holes and occurs on a timescale of *ca*. 5 orders of magnitude slower than hydrogen evolution (12, 29). OER over pure Ag₃PO₄ catalysts under simulated solar irradiation was tested for catalytic activity identification. As shown in Fig. 5*B*, Ag₃PO₄₍₁₁₁₎ tetrahedrons show the highest OER activity with a high initial rate of 3,925 µmol h⁻¹ g⁻¹, two times higher than that of the polyhedrons,



Fig. 5. Photocatalysis performance. (*A*) Tauc plots for determination of the band gap of Ag_3PO_4 semiconductor. (*B*) Photocatalytic OER performance, (*C*) comparison of OER efficiency between as-prepared $Ag_3PO_{4(111)}$ tetrahedrons and reported catalysts (50–58). (*D*) Photocatalytic nitrate formation at ambient conditions under simulated one solar irradiation. (*E*) Comparison of the direct nitrate photosynthesis efficiency from N₂ between as-prepared Ag_3PO_4 and reported catalysts. (59–63) (*F*) Schematic of faceted Ag_3PO_4 catalyst for water splitting and nitrogen fixation.

and over three times than irregular Ag_3PO_4 . Impressively, the OER efficiency of as-prepared $Ag_3PO_{4(111)}$ tetrahedrons outperforms the most reported catalysts (Fig. 5*C*) (50–58).

The designed Ag3PO4 with high-index facets may activate inert chemical bonds into high value-added chemicals. The Ag₃PO₄ catalyst was then used for direct nitrate synthesis from dinitrogen for the first time, which is an essential but extraordinarily difficult process owing to the very inert nonpolar N≡N covalent triple bond (59, 60). Impressively, nitrate was directly produced from N_2 upon the catalysis by faceted Ag₃PO₄ when purified air was purged into the reactor under one simulated solar irradiation (Fig. 5D). Blank control tests eliminated the interference of impurity from catalyst (SI Appendix, Fig. S16), confirming that the nitrate product was originating from the N2 conversion over Ag3PO4 catalyst. Of which, $Ag_3PO_{4(111)}$ tetrahedrons exhibit the highest N₂ conversion efficiency with the nitrate production rate of 58.7 μ mol h⁻¹ g⁻¹ compared with the polyhedrons and irregular Ag₃PO₄. The direct nitrate photosynthesis efficiency of the optimized Ag₃PO₄ outperforms the most reported catalysts (59-63), which is a green catalysis technology and even comparable to the mainstream electrocatalysis reported (Fig. 5*E*). More generally, these results for challenging catalytic reactions validate the effectiveness and potential of this crystal regulation strategy for practical catalytic applications. Additionally, the flexible PVDF/PTFE@Ag₃PO₄ heterostructure might be a potential floating photocatalyst for solar water treatment such as organic degradation, which could achieve piezoelectric-enhanced catalysis by the ferroelectret substrates (64).

To study the versatility of such an electrically tunable crystal growth strategy by dipole-sourced electrostatic filed, investigation of broadening catalyst synthesis scope was conducted. Herein, zinc oxide (ZnO) semiconductor crystal is chosen as the typical example using Zn²⁺ precursor, due to its wide applications in catalysis and energy storage (65). As shown in *SI Appendix*, Fig. S17*A* distinct structure and morphology variation was found in ZnO synthetic system. Significantly changed aspect ratio (length-diameter) of fusiform-like ZnO micro-crystals is observed using different PVDF/PTFE ferroelectret NFs, and a notable morphology variation from individual fusiform to combined urchin appearance with size evolution is found. XRD patterns reveal the

crystalline structure of ZnO products corresponding to wurtzite-type ZnO (JCPDS 79-0205). Obvious crystal structural evolution in the intensity ratios of main diffractions of (100), (002), and (101) peaks is observed, indicating crystal facet orientation. The realization of precise growth control of different crystal catalysts demonstrates the effectiveness and universality of such a growth strategy, which makes the controllable catalyst production simple and cost-efficient, especially for general ionic crystals.

Conclusions

In summary, we have developed a new and versatile structural engineering strategy for crystal growth regulation by introducing in situ dipole-sourced electrostatic field using ferroelectret. By varying the polar β-phase contents of PVDF-based ferroelectret NFs, a notable morphology evolution with different dominated facets of Ag₃PO₄ model catalyst is observed, in which free Ag₃PO₄ (sub)microcrystal turns to well-defined necklace-like Ag₃PO₄₍₁₁₁₎ tetrahedron grown on fibers, or multifaceted polyhedron with increasing polarization level. Theoretical calculations and simulation suggest that the induced electrostatic field plays an important role in faceted crystal growth, where the resultant electrostatic and dielectrophoretic force can effectively regulate the migration of Ag⁺ ions and free Ag₃PO₄ nuclei for competitive faceted growth, respectively. This strategy substantially simplifies the synthetic process and avoids the undesirable capping agents that decays catalytic reactivity, and the as-prepared catalysts emerge attractive performance for challenging catalytic reactions. As a proof of concept, the green and precise growth modulation of Ag₃PO₄ and ZnO catalysts, suggesting the feasibility of this electrically tunable growth concept by interfacial electrostatic field, brings more possibilities and new ideas for crystal structures design.

Methods

The chemicals and materials used in the experiments are described in SI Appendix.

Fabrication of PVDF/PTFE Ferroelectret Nanofibers. Electrospinning as an advanced fiber fabrication technology is effective to produce self-poled high stretching force exerted on electrified solution jets (31, 32). A direct current (DC) electric field was applied between the needle and collecting plate (Fig. 1A). During the electrospinning process, the polarization by high electric field and the stretching of shear field induces phase transformation from nonpolar α phase to ferroelectric polar β phase and dipole orientation of PVDF. And the direction of the dipoles is perpendicular to the molecular chains of PVDF in the β crystal (66, 67), because the ferroelectric polar β phase has the *trans-trans-trans-trans* (TTTT) conformation result from the separation of the CF₂ and CH₂ groups (Top Inset of Fig. 1A). It is also for this reason that β PVDF has the fascinating property (260. To further stabilize the phase and dipole orientation of PVDF, PTFE nanoparticles (NPs) were employed as an inspiring charge enhancer, because both of which are provided with substantial fluorine atoms and an extremely strong negative induction effect (26, 33–35). The positively charged -CH₂ groups in PVDF chains could incur strong intermolecular interactions with the negatively charged -CF₂ groups on PTFE via hydrogen bonds and dipole interactions (Right Inset of Fig. 1A). This long-range intermolecular interactions along the PVDF-PTFE interfaces not only promoted in situ nucleation of β -phase PVDF with aligned CH₂-CF₂ orientation chain (i.e., TTTT structure) (23) but also formed stable dipole charges. Specifically, the electrospinning solution was prepared by dissolving 10% mixed PVDF polymer and PTFE nanoparticles (30 to 50 nm, 0.05 wt % of PVDF) in a

ferroelectret PVDF nanofibers (NFs) with a high β -phase ratio because of the

mixed solvent of DMF/acetone. Ultrasonication was employed for 30 min to ensure the well-dispersion of PTFE NPs, and afterward the multicomponent solutions were subjected to vigorous stirring for 12 h at 55 °C to yield homogeneous dissolution of polymers. PVDF/PTFE ferroelectret nanofibers (NFs) were fabricated by far-field electrospinning equipment (Beijing Ucalery Technology Development Co., Ltd.). Typically, the PVDF/PTFE mixed solution was sucked into plastic syringes. Afterward, the solution was extruded through #21 metallic nozzle with a governable infusion velocity of 1 mL h⁻¹, and a high DC voltage was simultaneously carried out in the pinpoints of the nozzle, giving rise to the formation of a stable jet flow at 20 °C and 35% relative humidity. To further strengthen the regulation of the polarization degree of PVDF/PTFE ferroelectret, different DMF/acetone volume ratio of 3:0, 3:1, and 3:2, corresponding DC voltage strength of 0.75, 1, and 1.25 kV cm⁻¹, respectively, were adapted for electrospinning. The DMF/acetone solvent can change the surface tension and volatility of the spinning solution, which affects the PVDF/PTFE formation process. In addition, the acetone may be used as nucleating agent and change the PVDF crystallization kinetics (26, 68). Through the synergy of these two factors, the desirable the polarization level of PVDF/PTFE ferroelectret NFs can be achieved. The resultant NFs were dried in vacuum for further treatment, denoted as $\mathsf{PVDF/PTFE}_{\mathsf{low}}$ $\mathsf{PVDF/PTFE}_{\mathsf{mid}}$ and $\mathsf{PVDF/PTFE}_{\mathsf{high}}$ which represent the β phase polarization degree of PVDF/PTFE from low to high, respectively. Non-ferroelectret PAN NFs (10% PAN/DMF) were also fabricated for fair comparison.

Synthesis of PVDF/PTFE@Ag₃**PO**₄. The synthesis of faceted Ag₃PO₄ crystals was assisted by PVDF/PTFE NFs via a typical wet-chemistry method. In a typical synthesis, PVDF/PTFE NFs was firstly immersed in 20 mL of AgNO₃ (0.15 M) ethanol solution. Then 5 mL H₃PO₄ in 15 mL ethanol solution was added dropwise into above solution and held for 3 h. Afterward, the resultant PVDF/PTFE@Ag₃PO₄

- V. Andrei *et al.*, Floating perovskite-BiVO₄ devices for scalable solar fuel production. *Nature* 608, 518–522 (2022).
- Y. Zhao et al., Pulsed hydraulic-pressure-responsive self-cleaning membrane. Nature 608, 69–73 (2022).
- Z. Li, M. Saruyama, T. Asaka, Y. Tatetsu, T. Teranishi, Determinants of crystal structure transformation of ionic nanocrystals in cation exchange reactions. *Science* 373, 332–337 (2021).
- H. G. Yang et al., Anatase TiO₂ single crystals with a large percentage of reactive facets. Nature 453, 638–641 (2008).
- S. Rong, P. Zhang, F. Liu, Y. Yang, Engineering crystal facet of α-MnO₂ nanowire for highly efficient catalytic oxidation of carcinogenic airborne formaldehyde. ACS Catal. 8, 3435–3446 (2018).
- Y. Li *et al.*, Corner-, edge-, and facet-controlled growth of nanocrystals. *Sci. Adv.* 7, eabf1410 (2021).
 M. Song *et al.*, Crystal facet engineering of single-crystalline TiC nanocubes for improved hydrogen
- eolution reaction. Adv. Funct. Mater. 31, 2008028 (2020).
 Y. Qi et al., Nanocrystal facet modulation to enhance transferrin binding and cellular delivery. Nat. Commun. 11, 1262 (2020).
- K. J. Wu, E. C. M. Tse, C. Shang, Z. Guo, Nucleation and growth in solution synthesis of nanostructures-From fundamentals to advanced applications. *Prog. Mater. Sci.* **123**, 100821 (2021).
- B. Shen et al., Crystal structure engineering in multimetallic high-index facet nanocatalysts. Proc. Natl. Acad. Sci. U.S.A. 118, e2105722118 (2021).
- Y. Guo et al., Citric acid modulated growth of oriented lead perovskite crystals for efficient solar cells. J. Am. Chem. Soc. 139, 9598–9604 (2017).

was washed with ethanol several times and dried under vacuum. Additionally, the in situ grown of Ag₃PO₄ on PVDF/PTFE_{high} NFs was observed using dark-field optical microscopy (Zeiss Axioimager A2m, *SI Appendix*, Fig. S14). Pure Ag₃PO₄ crystal and PAN@Ag₃PO₄ were also synthesized for fair comparison. It is worth mentioning that the Ag₃PO₄ crystals grown on fibers was exfoliated/separated from substrate by mild ultrasound for photocatalytic applications to eliminate the heterostructure effect.

Synthesis of PVDF/PTFE@ZnO. The PVDF/PTFE@ZnO was prepared by the low-temperature hydrothermal synthesis technology. The prepared PVDF/PTFE fibers are pre-immersed into the 50 mL nutrient aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (30 mM) for 12 h. Afterward, hexamethylenetetramine (10 mM) was added above solution, which was sealed and placed in a 95 °C oven for 20 h. Finally, the samples were rinsed with a large amount of running DI water to remove the residue.

Surface Potential and Topography Maps of a Single Nanofiber. The surface potential and topography of the single nanofiber were undertaken by atomic force microscopy (AFM, NT-MDT). Single NF was produced by the electrospinning jet and directly loaded on to the indium-tin oxide (ITO) conductive glass. Under Kelvin Probe Force Microscopy [KPFM, a member of atomic force microscope (AFM) family] measurements, double path measurement was used, and the typical lift height was 10 nm. The topography and surface potential maps of samples were obtained by tapping mode scanning (carrying an NSG10 tip of TipsNano).

Besides, the zeta potentials of samples were collected by streaming potential measurement with the SurPASS3 electrokinetic analyzer (Anton Paar GmbH, Austria). PVDF/PTFE NFs membrane was cut into two 1 cm \times 2 cm pieces and fixed on flat sample table, followed by loading in the measurement instrument. Then 0.001 M KCl aqueous electrolyte is circulated through the sample-loaded measuring cell. Automatic titration with 0.1 M HCl and 0.1 M NaOH solutions was employed to control the pH values upon zeta potential measurement and thus determining the isoelectric point and surface potentials of samples.

Data, Materials, and Software Availability. All study data are included in the article and/or *SI Appendix*.

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- D. J. Martin, N. Umezawa, X. Chen, J. Ye, J. Tang, Facet engineered Ag₃PO₄ for efficient water photooxidation. *Energy Environ. Sci.* 6, 3380 (2013).
- Z. Chen, J. W. Chang, C. Balasanthiran, S. T. Milner, R. M. Rioux, Anisotropic growth of silver nanoparticles is kinetically controlled by polyvinylpyrrolidone binding. J. Am. Chem. Soc. 141, 4328–4337 (2019).
- L. F. Alexander, N. Radacsi, Application of electric fields for controlling crystallization. *CrystEngComm* 21, 5014–5031 (2019).
- O. Sato, Dynamic molecular crystals with switchable physical properties. Nat. Chem. 8, 644–656 (2016).
- M. Taleb et al., Crystallization of proteins under an external electric field. J. Cryst. Growth 200, 575–582 (1999).
- F. Li, R. Lakerveld, Electric-field-assisted protein crystallization in continuous flow. Cryst. Growth Des. 18, 2964–2971 (2018).
- 18. D. Hou, H.-C. Chang, AC field enhanced protein crystallization. *Appl. Phys. Lett.* **92**, 223902 (2008).
- C. Tang, X. Liao, W. Zhong, H. Yu, Z. Liu, Electric field assisted growth and field emission properties of thermally oxidized CuO nanowires. *RSC Adv.* 7, 6439–6446 (2017).
- P. D. Morris et al., Electric field-controlled synthesis and characterisation of single metal-organicframework (MOF) nanoparticles. Angew. Chem. Int. Ed. Engl. 59, 19696–19701 (2020).
- K. Qu et al., Electrostatic-induced crystal-rearrangement of porous organic cage membrane for CO₂ Capture. Angew. Chem. Int. Ed. Engl. 61, e202205481 (2022).
- Y. Zhang *et al.*, Ferroelectret materials and devices for energy harvesting applications. *Nano Energy* 57, 118–140 (2019).

- X. Zhang, P. Pondrom, G. M. Sessler, X. Ma, Ferroelectret nanogenerator with large transverse piezoelectric activity. *Nano Energy* 50, 52–61 (2018).
- Y. Sakane, Y. Suzuki, N. Kasagi, The development of a high-performance perfluorinated polymer electret and its application to micro power generation. J. Micromech. Microeng. 18, 104011 (2008).
- N. Mendel, H. Wu, F. Mugele, Electrowetting-assisted generation of ultrastable high charge densities in composite silicon oxide-fluoropolymer electret samples for electric nanogenerators. *Adv. Funct. Mater.* 31, 2007872 (2021).
- Z. Cui, N. T. Hassankiadeh, Y. Zhuang, E. Drioli, Y. M. Lee, Crystalline polymorphism in poly(vinylidenefluoride) membranes. *Prog. Polym. Sci.* 51, 94–126 (2015).
- A. G. Kravtsov, H. Brünig, S. F. Zhandarov, Analysis of the polarization state of melt-spun polypropylene fibers. J. Mater. Process. Tech. 124, 160–165 (2002).
- V. E. Kalayci, P. K. Patra, Y. K. Kim, S. C. Ugbolue, S. B. Warner, Charge consequences in electrospun polyacrylonitrile (PAN) nanofibers. *Polymer* 46, 7191–7200 (2005).
- Z. Yi et al., An orthoposphate semiconductor with photooxidation properties under visible-light irradiation. Nat. Mater. 9, 559–564 (2010).
- D. J. Martin *et al.*, Efficient visible driven photocatalyst, silver phosphate: Performance, understanding and perspective. *Chem. Soc. Rev.* 44, 7808–7828 (2015).
- T. Li et al., High-performance poly(vinylidene difluoride)/dopamine core/shell piezoelectric nanofiber and its application for biomedical sensors. Adv. Mater. 33, e2006093 (2021).
- H. Shao, J. Fang, H. Wang, T. Lin, Effect of electrospinning parameters and polymer concentrations on mechanical-to-electrical energy conversion of randomly-oriented electrospun poly(vinylidene fluoride) nanofiber mats. RSC Adv. 5, 14345–14350 (2015).
- Y. Wang *et al.*, Ultrasonic activation of inert poly(tetrafluoroethylene) enables piezocatalytic generation of reactive oxygen species. *Nat. Commun.* 12, 3508 (2021).
- S. Wang, X. Zhao, X. Yin, J. Yu, B. Ding, Electret polyvinylidene fluoride nanofibers hybridized by polytetrafluoroethylene nanoparticles for high-efficiency air filtration. ACS Appl. Mater. Inter. 8, 23985–23994 (2016).
- F. Calavalle et al., Piezoelectric and electrostatic properties of electrospun PVDF-TrFE nanofibers and their role in electromechanical transduction in nanogenerators and strain sensors. *Macromol. Mater.* Eng. 305, 2000162 (2020).
- P. Thakur *et al.*, Superior performances of in situ synthesized ZnO/PVDF thin film based self-poled piezoelectric nanogenerator and self-charged photo-power bank with high durability. *Nano Energy* 44, 456–467 (2018).
- W. Wu et al., Water flow drived piezo-photocatalytic flexible films: Bi-piezoelectric integration of ZnO nanorods and PVDF. Appl. Surf. Sci. 517, 146119 (2020).
- 38. B. Zheng *et al.*, High-efficiently visible light-responsive photocatalysts: Ag3PO4 tetrahedral
- microcrystals with exposed 111 facets of high surface energy. J. Mater. Chem. A 1, 12635 (2013).
 J. Ke et al., Facet-dependent electrooxidation of propylene into propylene oxide over Ag₃PO₄ crystals. Nat. Commun. 13, 932 (2022).
- Y. Bi, S. Ouyang, N. Umezawa, J. Cao, J. Ye, Facet effect of single-crystalline Ag₃PO₄ sub-microcrystals on photocatalytic properties. J. Am. Chem. Soc. **133**, 6490–6492 (2011).
- M.-S. Hsieh, H.-J. Su, P.-L. Hsieh, Y.-W. Chiang, M. H. Huang, Synthesis of Ag₃PO₄ crystals with tunable shapes for facet-dependent optical property, photocatalytic activity, and electrical conductivity examinations. ACS Appl. Mater. Interfaces 9, 39086–39093 (2017).
- E. Curcio, E. Fontananova, G. Di Profio, E. Drioli, Influence of the structural properties of poly(vinylidene fluoride) membranes on the heterogeneous nucleation rate of protein crystals. J. Phys. Chem. B 110, 12438–12445 (2006).
- A. Luditskiy, Y. Xia, Toward the synthesis of sub-15 nm Ag nanocubes with sharp corners and edges: The roles of heterogeneous nucleation and surface capping. J. Am. Chem. Soc. 138, 3161–3167 (2016).
- N. E. Chayen, E. Saridakis, R. P. Sear, Experiment and theory for heterogeneous nucleation of protein crystals in a porous medium. *Proc. Natl. Acad. Sci. U.S.A.* **103**, 597–601 (2006).

- G. R. Pesch, F. Du, A review of dielectrophoretic separation and classification of non-biological particles. *Electrophoresis* 42, 134–152 (2021).
- F. Li, R. Lakerveld, Influence of alternating electric fields on protein crystallization in microfluidic devices with patterned electrodes in a parallel-plate configuration. *Cryst. Growth Des.* 17, 3062–3070 (2017).
- Q. Yao et al., Counterion-assisted shaping of nanocluster supracrystals. Angew. Chem. Int. Ed. Engl. 54, 184–189 (2015).
- M. A. Butler, Photoelectrolysis and physical properties of the semiconducting electrode WO₂. J. Appl. Phys. 48, 1914–1920 (1977).
- M. Pan, H. Zhang, G. Gao, L. Liu, W. Chen, Facet-dependent catalytic activity of nanosheet-assembled bismuth oxyiodide microspheres in degradation of bisphenol A. *Environ. Sci. Technol.* 49, 6240–6248 (2015).
- R. Pan et al., Two-dimensional all-in-one sulfide monolayers driving photocatalytic overall water splitting. Nano Lett. 21, 6228–6236 (2021).
- C. M. Wolff et al., All-in-one visible-light-driven water splitting by combining nanoparticulate and molecular co-catalysts on CdS nanorods. Nat. Energy 3, 862–869 (2018).
- C. Wu et al., Mesoporous polymeric cyanamide-triazole-heptazine photocatalysts for highly-efficient water splitting. Small 16, e2003162 (2020).
- W. Fu, X. Guan, Z. Huang, M. Liu, L. Guo, Efficient photocatalytic overall water splitting over a coreshell GaInZnON@GaInON homojunction. *Appl. Catal. B* 255, 117741 (2019).
- L. Ren et al., Nitrogen-doped ultrathin graphene encapsulated Cu nanoparticles decorated on SrTiO₃ as an efficient water oxidation photocatalyst with activity comparable to BiVO₄ under visible-light irradiation. Appl. Catal. B 279, 119352 (2020).
- L. Wang *et al.*, Boosting NIR-driven photocatalytic water splitting by constructing 2D/3D epitaxial heterostructures. J. Mater. Chem. A 7, 13629–13634 (2019).
- D. Zhao et al., Synergy of dopants and defects in graphitic carbon nitride with exceptionally modulated band structures for efficient photocatalytic oxygen evolution. Adv. Mater. 31, e1903545 (2019).
- P. Li *et al.*, Polyhedral 30-faceted BiVO₄ microcrystals predominantly enclosed by high-index planes promoting photocatalytic water-splitting activity. *Adv. Mater.* **30**, 1703119 (2018).
- Y. Li *et al.*, In situ synthesis of a novel Mn₃O₄/g-C₃N₄ p-n heterostructure photocatalyst for water splitting. *J. Colloid Interface Sci.* 586, 778–784 (2021).
- Y. Liu et al., Pothole-rich ultrathin WO₃ nanosheets that trigger N≡N bond activation of nitrogen for direct nitrate photosynthesis. Angew. Chem. 58, 731–735 (2018).
- S. J. Yuan et al., Nitrate formation from atmospheric nitrogen and oxygen photocatalysed by nanosized titanium dioxide. Nat. Commun. 4, 2249 (2013).
- J. Yang et al., Photodriven disproportionation of nitrogen and its change to reductive nitrogen photofixation. Angew. Chem. Int. Ed. Engl. 60, 927–936 (2021).
- Y. Yu *et al.*, A nitrogen fixation strategy to synthesize NO via the thermally assisted photocatalytic conversion of air. *J. Mater. Chem. A* 8, 19623–19630 (2020).
- X. Gao et al., Enhanced photocatalytic N₂ fixation by promoting N₂ adsorption with a co-catalyst. Sci. Bull. 64, 918–925 (2019).
- S. Tu et al., Piezocatalysis and piezo-photocatalysis: Catalysts classification and modification strategy, reaction mechanism, and practical application. Adv. Funct. Mater. 30, 2005158 (2020).
- S. Song et al., A selective Au-ZnO/TiO2 hybrid photocatalyst for oxidative coupling of methane to ethane with dioxygen. Nat. Catal. 4, 1032-1042 (2021).
- D. Lolla et al., Polyvinylidene fluoride molecules in nanofibers, imaged at atomic scale by aberration corrected electron microscopy. Nanoscale 8, 120–128 (2016).
- J. Miao, D. H. Reneker, M. Tsige, P. L. Taylor, Molecular dynamics simulations and morphology analysis of TEM imaged PVDF nanofibers. *Polymer* 125, 190-199 (2017).
- Y. J. Hwang, S. Choi, H. S. Kim, Structural deformation of PVDF nanoweb due to electrospinning behavior affected by solvent ratio. *e-Polymers* 18, 339–345 (2018).