

Highly Efficient Flexocatalysis of Two-Dimensional Semiconductors

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Catalysis is vitally important for chemical engineering, energy, and environment. It is critical to discover new mechanisms for efficient catalysis. For piezoelectric/pyroelectric/ferroelectric materials that have a noncentrosymmetric structure, interfacial polarization-induced redox reactions at surfaces leads to advanced mechanocatalysis. Here, the first flexocatalysis for 2D centrosymmetric semiconductors, such as MnO₂ nanosheets, is demonstrated largely expanding the polarization-based-mechanocatalysis to 2D centrosymmetric materials. Under ultrasonic excitation, the reactive species are created due to the strain-gradient-induced flexoelectric polarization in MnO₂ nanosheets composed nanoflowers. The organic pollutants (Methylene Blue et al.) can be effectively degraded within 5 min; the performance of the flexocatalysis is comparable to that of state-of-theart piezocatalysis, with excellent stability and reproducibility. Moreover, the factors related to flexocatalysis such as material morphology, adsorption, mechanical vibration intensity, and temperature are explored, which give deep insights into the mechanocatalysis. This study opens the field of flexoelectric effect-based mechanochemistry in 2D centrosymmetric semiconductors.

1. Introduction

Mechanocatalysis is an emerging area toward advanced catalysis without energy input either light or electricity. The mechanochemical activation catalyst uses mechanical trigger

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as the driving force to induce physical or chemical electron transfer process for stimulating catalysis.^[1-3] Since the mechanocatalysis was first introduced,^[4] it has been extensively exploited in various areas, such as material synthesis,^[5] water treatment,^[6] recycling, or other radicals-related chemistry.^[7] In recent years, using surface polarization charges of a piezoelectric/ pyroelectric/ferroelectric semiconductor, the piezocatalysis, a new type of mechanocatalysis, has been reported that can directly achieve electrochemical reaction by mechanical stimuli.^[8] The polarization of the deformed piezoelectric/pyroelectric/ ferroelectric semiconductor can augment the energetics of both free and bound charges, and promote the separation of carriers and increase the life time of excited charges that participate in the catalytic reactions.^[9,10] Piezocatalysis can utilize not only the mechanical vibrations in the environment such as wind or waves.

but also the redundant vibrations in industrial systems for catalytic activity. Thus, the piezocatalysis is considered as a promising green mechanocatalysis. However, the piezoelectric, pyroelectric, or ferroelectric effect only manifest in piezoelectric materials that have non-centrosymmetric structures, for example, the wurtzite structure,^[11] which greatly



limits the choice of materials for piezocatalysis and its applications, especially in the low-dimensional centrosymmetric semiconductors such as 1D nanowire/nanotube and 2D nanosheets.

Flexoelectricity is an electromechanical property of a dielectric material, which makes materials to exhibit an electrical polarization induced by inhomogeneous strain.^[12,13] In centrosymmetric crystals, the strain-gradient can break their local inversion symmetry, generating an electrical polarization with a preferred direction and enabling a piezoelectric-like response. Coupling the flexoelectricity and the semiconducting property of a crystal, new electronic/optoelectronic phenomena in nonpiezoelectric semiconductors have been discovered such as giant flexoelectric effect,^[14] flexo-photovoltaic effect,^[15] flexoelectronics, and photoflexoelectric effect.^[16,17] In general, although the flexoelectric effect in bulk crystals is negligible due to the small strain-gradient ($\approx 0.1 \, \text{m}^{-1}$) under mechanical bending state,^[18] large strain-gradient (10⁶-10⁹ m⁻¹) and corresponding flexoelectric response can be generated in thin flakes by nanoindentation,^[19] mechanical bending,^[20] and dislocation et al.^[21] In the past reports, the role of the large strain-gradient-induced flexoelectric polarization of 2D nanosheets is always overlooked in the mechanocatalysis. Actually, it may enable promising polarization-based mechanocatalysis with high efficiency in 2D centrosymmetric materials.

Here, we report the first study of flexoelectric catalysis (flexocatalysis) in 2D centrosymmetric semiconductors, a new catalytic mechanism, which demonstrate that the polarizationbased mechanocatalysis can be induced in 2D centrosymmetric nanosheets by mediation of the flexoelectricity. The dynamic flexoelectric polarization of MnO2 nanoflowers integrated by 2D nanosheets under ultrasonic stimulation can sustainably drive the redox reactions and effectively degrade organic pollutants, which exhibits high efficiency, excellent stability, and reproducibility. The performance of the flexocatalysis in MnO2 nanoflowers is comparable to that of the state-of-the-art piezocatalysis (using various piezoelectric materials, such as MoS₂, ZnS, and Bi₂WO₆, Table S1, Supporting Information). In addition, factors related to the flexocatalysis such as material morphology, adsorption, the magnitude of the mechanical stimuli, and temperature have been investigated systematically. Our study largely expands the piezocatalysis to all symmetry classes of 2D semiconductors, showing great potential of dynamic flexoelectric polarization of 2D centrosymmetric semiconductors for highly efficient mechanocatalysis and mechanochemistry.

2. Results and Discussion

2.1. Mechanism of the Flexocatalysis in Two-Dimensional Centrosymmetric Semiconductors

To demonstrate our idea, we constructed nanoflowers by integrating 2D centrosymmetric nanosheets at first (**Figure 1**a). Each nanosheet can be considered as a cantilever beam, which is easily deformed under mechanical vibration. It should be noted that the nanoflower does not a specific material, but represents semiconductors that have the nanoflower-like structure. When applied an inhomogeneous strain to the nanosheet, the center of the cations

and the center of anions are relatively displaced, resulting in a flexoelectric polarization (Figure 1b), which is the origin of the flexoelectricity. Here we use ultrasonic wave as the mechanical excitation source (40 kHz), which can generate a pressure of 10⁵-10⁶ Pa in the liquid environment.^[22] It can even release a peak pressure of 10⁸–10⁹ Pa and act on the surroundings when the cavitation bubbles generated by ultrasound reach the critical rupture size.^[23,24] The spatial strain distribution of each nanosheet under the pressure with same magnitude as that produced by ultrasonic wave can be calculated analytically (Experimental Section). As can be seen, the strain-gradient of 2D nanosheet is as large as 10⁷ (Figure 1c and Figure S1, Supporting Information), which is much larger than those achievable using conventional beambending approaches (in the range of 10⁻¹–10² m⁻¹).^[25,26] The outof-plane flexoelectric polarization (P) are induced throughout the whole nanosheet, with a maximum value of about 0.02 Cm⁻² (Figure 1d), which is comparable to that of crystal under nanoindentation. The experimental values may be orders of magnitude higher than the simulated result, which has been proved in previous studies.^[27] These results demonstrate that large strain-gradient will generate in the nanoflower integrated by 2D nanosheets under ultrasonic irradiation, resulting in effective flexoelectric polarization within itself (Figure 1a).

Figure 1e shows the proposed mechanism of the flexocatalysis in 2D centrosymmetric semiconductors. Reactive species such as •OH and $\cdot O_2^{-}$, are the key for the flexocatalysis, which is generally produced through reducing oxygen and oxidizing hydroxyl. However, without external mechanical trigger, the redox reactions almost cannot automatically take place (Figure S2, Supporting Information). On the one hand, the concentration of free carriers (electrons and holes) within the nanosheet is limited, and more importantly, these carriers cannot be separated to participate in the redox reaction. Under periodical ultrasonic irradiation, the dynamic flexoelectric polarization (P_{flexo}) will be created throughout the whole nanosheets, which has a huge impact on the concentration and distribution of free carriers, resulting in band-structure engineering of the whole crystal. It can act as a strong force to drive electrons and holes moving in the opposite direction, thereby achieving efficient separation of free carriers and causing the energy band to be completely tilted (Figure 1e[i]). Owing to the nanometer thickness and large surface area of the nanosheet, these carriers can be easily transported into the catalyst surfaces (Equation (1)) and combine with water and oxygen molecules to further generate reactive species of $\cdot OH$ and $\cdot O_2^{-1}$ (Equations (2) and (3)). The reactive species can degrade organic dyes into small molecules (Equation (4)). The carriers consumed by the redox reactions can be reproduced by thermal excitation via absorbing the mechanical energy of ultrasonic irradiation. Due to the high frequency of ultrasonic wave, the mechanical vibration-induced dynamic flexoelectric polarization in 2D centrosymmetric nanosheets cannot be fully screened. Therefore, it can continuously produce the reactive species, so as to control the catalytic process (Figure 1e[ii]), which is analogous but different to the piezocatalysis in various piezoelectric materials.^[28] The magnitude of the dynamic flexoelectric polarization and the rate of flexocatalysis of 2D centrosymmetric nanosheets depend on the magnitude and frequency of the applied mechanical stimuli. This is the flexocatalysis, which is ubiquitous, persistent, and widespread in 2D semiconductors regardless of its crystal





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Figure 1. The mechanism of the flexocatalysis in 2D centrosymmetric semiconductor. a) Schematic showing the nanoflower-like structure integrated by 2D nanosheets under strain-free and ultrasonic irradiation condition. Each nanosheet can be considered as a cantilever beam, which is easily deformed under mechanical vibration. b) Flexoelectricity of 2D centrosymmetric materials with inhomogeneous strain. When applying an inhomogeneous strain to the nanosheet, the center of the cations and the center of anions are relatively displaced, resulting in a flexoelectric polarization over the whole nanosheet. c,d) Flexoelectricity in 2D materials obtained by the theoretical simulation with a cantilever beam model, showing the corresponding strain distribution (c) and the flexoelectric polarization distribution (d) under a force of 100 nN. e) Schematic showing the proposed mechanism of flexo-catalysis for organic pollutants degradation: (i) the generation of inner crystal flexoelectric polarization resulting in the band-structure engineering. CB, VB, and E_F represent the conduction band, valence band, and Fermi surface, respectively. The black and orange lines represent the band structures of 2D semiconductor without and with strain-gradient, respectively; (ii) the process of separation and transportation of electrons and holes and the generation of reactive species that participate in the degradation process of organic pollutants.

structure owing to its 2D morphology, semiconducting property, and large flexoelectric response.

 $MnO_2 + Vibration \rightarrow MnO_2(h^+ + e^-)$ (1)

 $H_2O + h^+ \rightarrow \bullet OH$ (2)

 $O_2 + e^- \to \bullet O_2^- \tag{3}$

Organic Dye+ $\bullet O_2^-$ or $\bullet OH \rightarrow Degradation Production$

2.2. Characterization of Centrosymmetric MnO₂ Nanoflowers

Next, we synthesized MnO₂ nanoflowers by hydrothermal method (Note S1, Supporting Information). The X-ray diffraction (XRD) spectrum clearly shows that the diffraction peaks at $2\theta = 12.30^{\circ}$, 25.12°, 36.65°, and 66.96° are well assigned to the (001), (002), (111), and (114) planes of birnessite-type manganese oxide structure,^[29] indicating that the synthesized sample is δ MnO₂ without other crystalline impurities (**Figure 2**a). The

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Figure 2. Performance of the flexocatalysis of centrosymmetric MnO_2 nanoflowers. a) The X-ray diffraction spectrum of MnO_2 nanoflowers, indicating that the synthesized sample is δMnO_2 . The inset is basic unit of δMnO_2 indicating that the δMnO_2 composed of edge-shared [MnO₆] octahedral belong to 2/m point group and has a centrosymmetric structure. b) The SEM image showing a typical morphology of MnO_2 nanoflower with multibranch hierarchical 2D nanosheets before flexocatalysis. c) The absorption spectra of MB solution with MnO_2 nanoflowers (5 mg) under ultrasonic irradiation (320 W, 40 kHz) treatment in dark. d) Degradation of MB solution as a function of ultrasonic irradiation time in the presence of MnO_2 nanoflowers showing the excellent stability and reproducibility of the flexocatalysis. f) The SEM images of MnO_2 nanoflowers after five cycles of the catalytic process.

single-crystalline nature of the δ -MnO₂ is further confirmed by the high-resolution transmission electron microscopy (HRTEM) (Figure S3b–f, Supporting Information). The basic unit of δ -MnO₂ is a MnO₆ octahedral with a single twofold rotation axis and perpendicular to the mirror plane (the inset of Figure 2a).^[30] The δ -MnO₂ composed of edge-shared [MnO₆] octahedral belong to 2/*m* point group and hence is centrosymmetric,^[31] which excludes the piezoelectric effect and facilitates the flexoelectric analysis. The synthesized MnO₂ possess a typical morphology of nanoflower with multi-branch hierarchical 2D nanosheets (Figure 2b and Figure S3a, Supporting Information), which is helpful to contribute effective flexoelectric response. The semiconducting property and the special flowerlike structure of δ -MnO₂ are beneficial to achieve efficient flexoelectrochemical performance driven by mechanical excitation.

2.3. The Performance of Flexocatalysis in Centrosymmetric MnO_2 Nanoflowers

We characterized the degradation capability of MnO₂ nanoflowers on target pollutant (Methylene Blue, MB) under ultrasonic vibration in dark. The water is kept at room temperature by the circulating cooling system. For comparison, the selfdegradation without catalyst and the degradation ability of MnO₂ nanoparticles were also assessed at the same experimental condition. The results show that MnO₂ nanoflowers possess the best catalytic activity. The degradation of MB solution is up to 98% after ultrasonic irradiation for 30 min (Figure 2c,d), largely outperforming most of the piezocatalysis (35–330 min, Table S1, Supporting Information). No degradation of MB can be detected without catalyst, and just a slight

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degradation happened in the presence of MnO2 nanoparticles with various amounts (1-50 mg) (Figure 2d and Figures S4 and S5, Supporting Information). It indicates that the selfdegradation of MB can be ignored and the possible effects of contact-electro-catalysis and oxidation of MnO2 do not play a major role here,^[32,33] because contact-electro-catalysis and the oxidation of material itself are supposed to occur for any shape of nanomaterials. Moreover, the electron paramagnetic resonance spectrums of active radicals ($\cdot O_2^-$ and $\cdot OH$) produced by MnO₂ were characterized (Figure S6, Supporting Information), which powerfully demonstrate that the MnO₂ nanoflowers under mechanical vibration can effectively produce active radicals. The optimized amount of MnO2 nanoflowers was also studied by taking catalyst with various amounts (1, 5, 10, 20, and 50 mg) into 50 mL (10 mg L⁻¹) MB dye solution under ultrasonic irradiation in dark. The catalyst with an amount of more than 1 mg exhibit strong degradation activity, and perform the best at around 5 mg (Figure S7, Supporting Information), which denote that the MB is not absorbed by the nanoflowers but degraded by the reactive species induced by the flexoelectric polarization. These results indicate that the dynamic flexoelectric polarization induced by ultrasonic irradiation through the flexoelectric effect of MnO2 nanoflowers is the key to achieve the efficient mechanocatalysis.

The stability and reproducibility of flexocatalysis in MnO₂ nanoflowers were evaluated by characterizing their cyclic property. After each cycle, the catalyst was recovered via centrifugation, washing, drying, and then re-added to fresh MB aqueous solution at the same experimental condition. Figure 2e and Figure S8, Supporting Information, shows that the organic pollutants are almost completely degraded within 30 min in each cycle. After five cycles of catalysis, there is only a slight (≈2%) decrease in the catalytic activity, which may be due to the incomplete catalyst recovery, since the amount of 5 mg is very small. This hypothesis can also be demonstrated by another phenomenon. The morphology of MnO2 nanoflowers hardly changes at all and the surfaces still remain clear without impurities after five cycles (ultrasonic irradiation for 20 h) of catalytic process (Figure 2f). These results indicate excellent stability and reproducibility of the flexocatalysis in MnO₂ nanoflowers. To show that the flexocatalysis is not limited to a certain pollutant, we performed the same experiments by using other typical organic pollutants, Rhodamine B(RhB) and Methyl Orange (MO). As expected, they can be degraded effectively to a certain extent, but the catalytic rate is less than that of MB (Figure S9, Supporting Information). The effectiveness, stability, and universality of the flexocatalysis are mainly attributed to the semiconductor property, 2D structure, and large flexoelectric response of MnO₂ nanoflowers.

2.4. The Influence of Adsorption on the Flexocatalysis

Adsorption is one of the key steps in heterogeneous catalytic reactions. It is generally thought that the catalyst and the reactant need to be fully contacted at first, to achieve an adsorption–desorption equilibrium.^[34] However, we found that the pre-adsorption process not only can not improve the performance of the flexocatalysis, but will result in a negative effect.



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Figure 3. The influence of adsorption on the flexocatalysis. Degradation of MB solution as a function of ultrasonic irradiation time in the presence of MnO_2 nanoflowers without the pre-adsorption process, and with pre-adsorption process of stirring for different time.

Here, we mix the MnO_2 nanoflowers and the MB solution and stirring for different time (15, 30, 45, and 60 min). As expected, there is a strong adsorption phenomenon in the mixed solution with a large amount of organic pollutants adsorbed on the surfaces of MnO_2 nanoflowers. The adsorption effect is more intense with the increase of stirring time (Figure S10, Supporting Information).

Next, we evaluated the degradation ability of MnO2 nanoflowers in the mixed solution after pre-adsorption processes with different stirring time. Other experimental conditions of the mechanocatalysis are the same with above section. The results show that the degradation ability of nanoflowers after the pre-adsorption process is significantly weakened compared with that without stirring (Figure 3 and Figures S11-S14, Supporting Information). With the increase of stirring time, the degradation ability of the nanoflowers in mixed solution gradually becomes weakened. Moreover, we found an interesting phenomenon in the degradation process with a pre-stirring for 60 min. When ultrasonic irradiation is applied, the intensity of absorption spectra curves shows a trend of increasing first and then decreasing gradually. It indicates that the organic pollutants adsorbed on the surfaces of the nanoflowers are redispersed into the solution under ultrasonic vibration, and then are gradually degraded by the reactive species. We proposed the mechanism of the weakened flexocatalysis after pre-adsorption process. On the one hand, the deformation of the nanosheets will be substantially decreased under ultrasonic excitation, owing to the adsorption of a large number of organic pollutants on the surfaces, which result in a weakened flexoelectric polarization. On the other hand, the contact area of nanoflowers with surroundings is significantly reduced, which severely hinders the attraction/release processes of free charges from surroundings in solution, inhibits the electron transfer process and hence the generation of reactive species that participate in dye degradation. These results give us a new insight into the role

of adsorption in the mechanocatalytic process, further demonstrating the dominant role of flexoelectric polarization in the flexocatalytic process.

2.5. The Influence of Mechanical Vibration Strength on the Flexocatalysis

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The magnitude of the flexoelectric polarization of nanosheet depends on the magnitude of the applied mechanical stimuli. To gain an insight into the dynamics of the flexocatalysis, we performed the degradation experiments under different ultrasonic power (320, 480, 640, and 800 W) but keep the temperature constant (20 °C) via circulating cooling system. **Figure 4**a–e shows that the MB solution degradation rate rapidly accelerated with increasing ultrasonic power. Especially, the pollutant is completely degraded within 5 min under an ultrasonic power of 800 W, the catalytic performance of which is comparable to the current state-of-the-art piezocatalysis (1–330 min, Table S1, Supporting Information).^[35,36] The improved flexocatalytic performance is mainly attributed to the enhanced redox reaction resulting from the larger effective flexoelectric polarization.

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Figure 4. The influence of ultrasonic power on the flexocatalysis. a–d) The absorption spectra of MB solution in the presence of MnO_2 nanoflowers under ultrasonic irradiation with different power (320, 480, 640, and 800 W). The insets show the corresponding photographs of MB dye solutions after catalytic processes. e) Degradation of MB solution as a function of ultrasonic irradiation time in the presence of MnO_2 nanoflowers with different ultrasonic power. f) The morphology of MnO_2 nanoflowers after the catalytic processes under ultrasonic irradiation with different power. The scale bars represent 500 nm. g) The cyclic degradation of MB solution in the presence of MnO_2 nanoflowers under high ultrasonic power of 800 W. h) The morphology of MnO_2 nanoflowers after each cycle showing that the flower-like structure of MnO_2 is severely damaged after five cycles. The scale bars represent 500 nm. i) The degradation MB solution in the presence of MnO_2 nanoparticles under different ultrasonic power. j) The degradation of MB solution with high power. All the catalytic degradation experiment were conducted under dark environment and kept at room temperature by the circulating cooling system.



Nevertheless, the excessive ultrasonic power may induce a negative effect on the flexocatalysis. The morphology of MnO_2 nanoflowers after degradation processes under different ultrasonic power was characterized, which show that the flower-like structure of MnO_2 is gradually destroyed with the increase of ultrasonic power and some floccules appear on the surfaces of nanoflowers (Figure 4f). Owing to the impurity of the degraded solution induced by the small floccules, the absorption intensity of the degraded solution gradually increased in wavelength range of 400–550 nm, and the color of the degraded solution gradually changed from clear to brown (Figure 4d).

To further understand the effect of ultrasonic power on the flexocatalysis, we evaluated the cyclic catalysis property of MnO₂ nanoflowers under high ultrasonic power (800 W). The degradation rate of MB significantly decreases after each cycle, with about 70% after the first cycle and about 80% after five cycles (Figure 4g and Figure S15, Supporting Information). We characterized the morphology of MnO₂ nanoflowers after each cycle. Figure 4h show that the flower-like structure of MnO₂ is severely damaged after each cycle, completely turning nanoflowers into nanoparticles after five cycles. Thus, the flexoelectric polarization of MnO2 nanoflowers will gradually weaken and eventually disappear, resulting in a serious decrease in the mechanocatalytic performance. Other factors that may arise from high ultrasonic irradiation have been excluded through the comparative experiments of using commercial MnO₂ nanoparticles as the catalyst or without catalyst under high ultrasonic power (Figure 4i,j and Figures S16 and S17, Supporting Information).

2.6. The Influence of Temperature on the Flexocatalysis

The reaction temperature is another important factor in catalysis.^[37] In this work, we kept the water temperature constant through the circulating cooling system. Nevertheless, considering that the inevitable fluctuations of reaction temperature caused by ultrasonic irradiation, we explore the role of temperature on the flexocatalysis. First, the degradation on pollutants without catalyst at high temperature (70 °C) was assessed. No obvious degradation of pollutants is observed, excluding the self-degradation of MB at high temperature (Figure 5j and Figure S18, Supporting Information). Next, we evaluated the degradation ability of MnO2 nanoflowers under different temperature (20, 30, 50, and 70 °C) and fixed the ultrasonic power. The results show that with the increase of temperature, the degradation performance is significantly improved (Figure 5a-e). Specifically, the MB is completely degraded within 5 min at 70 °C, which is promising for the design of highly efficient flexocatalysis at relative high temperature. The enhanced flexocatalysis may be due to the increase in carrier concentration within MnO₂ by thermal activation and the stronger inter-species reactivity.

However, similar to the case under high ultrasonic power, the excessive temperature may also have a negative effect on the flexocatalysis. We found that some floccules started to appear on the nanoflowers after catalytic process at 50 $^{\circ}$ C, and the flower-like structure was partially destroyed at 70 $^{\circ}$ C

(Figure 5f). Additionally, the cyclic degradation of MnO_2 nanoflowers on MB was performed at 70 °C. The result shows that the degradation ability substantially decreases after each cycle, with a reduction of more than 70% after five cycles (Figure 5g and Figure S19, Supporting Information). The morphology of MnO_2 nanoflowers after each cycles were characterized, of which the flower-like structure gradually disintegrates owing to the stronger action of cavitation bubbles enhanced by the increased temperature (Figure 5h). Hence, the flexocatalysis will become invalid owing to the disappearance of flexoelectric polarization in the nanoparticle, which has been further confirmed via the comparative experiments using MnO_2

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3. The Relationship between the Flexocatalysis and the Piezocatalysis

and Figure S20, Supporting Information).

nanoparticles as the catalysis at high temperature (Figure 5i

Flexocatalysis differs from, but is closely related to the piezocatalysis. Both of them use the polarization to generate reactive species at surfaces for the mechanocatalytic process. However, the piezocatalysis based on the piezoelectric effect only exists in piezoelectric/pyroelectric/ferroelectric materials that have a special non-centrosymmetric crystal structure such as the wurtzite structure.^[11] whereas the flexocatalysis driven by inhomogeneous strain-induced flexoelectric effect can be realized in any 2D semiconductors regardless of its crystal structure. Additionally, the piezoelectric polarization charge only presented within one or two atomic layers of a piezoelectric material, while the flexoelectric polarization is distributed throughout the crystal. Generally, the magnitude of the piezoelectric effect is much more effective than the flexoelectric effect. Nevertheless, large strain-gradient and corresponding flexoelectric response can be generated in 2D nanosheets by mechanical bending, which is even comparable to that of the piezoelectric effect. In 2D semiconductor, for example, the typical transition metal dichalcogenides (MoS₂, WS₂, et al.), the piezoelectric polarization charges are only distributed at the edges,^[38] while the flexoelectric polarization charges are distributed among the entire surfaces of 2D materials when it is deformed. Thus, the high performance of the piezocatalysis based on 2D piezoelectric semiconductors (Table S1, Supporting Information) may not only be attributed to the effect of piezoelectricity, but also the flexoelectricity. In other words, those materials exhibiting piezocatalysis also exhibit flexocatalysis, especially in 2D materials.

4. Conclusion

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To summarize, we developed the flexocatalysis for 2D centrosymmetric semiconductors, largely expanding the polarization-based-mechanocatalysis from non-centrosymmetric materials into 2D centrosymmetric semiconductors. The dynamic flexoelectric polarization of nanosheet composed nanoflowers induced by ultrasonic stimulation can sustainably drive the redox reactions and effectively degrade organic pollutants, which exhibits high efficiency, high stability, and



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Figure 5. The influence of temperature on the flexocatalysis. a–d) The absorption spectra of MB solution in the presence of MnO_2 nanoflowers under ultrasonic irradiation at different temperature (20, 30, 50, and 70 °C). The insets show the corresponding photographs of MB dye solutions after catalytic processes. e) Degradation of MB solution as a function of ultrasonic irradiation time in the presence of MnO_2 nanoflowers at different temperature. f) The morphology of MnO_2 nanoflowers after the catalytic processes under ultrasonic irradiation at different temperature. The scale bars represent 500 nm. g) The cyclic degradation of MB solution in the presence of MnO_2 nanoflowers under ultrasonic irradiation with a high temperature of 70 °C. h) The morphology of MnO_2 nanoflowers after each cycle showing that the flower-like structure of MnO_2 is severely damaged after five cycles. The scale bars represent 500 nm. i) The degradation MB solution in the presence of MnO_2 nanoparticles under ultrasonic irradiation at different temperature. j) The degradation without catalysts under ultrasonic irradiation at high temperature. All the catalytic degradation experiment were conducted under dark environment and fixed ultrasonic power.

reproducibility. The performance of the flexocatalysis in MnO_2 nanoflowers is comparable to that of the state-of-the-art piezocatalysis. The factors related to the flexocatalysis such as material morphology, adsorption, mechanical vibration strength, and temperature have been explored, which provide new insights into the mechanism of flexocatalysis. The effectiveness and universality of the flexocatalysis show promise for highly efficient mechanocatalytic application. This study is also a new extension of flexoelectricity to electrochemical functionality, which has the potential to excite new flexoelectric-based mechanochemical phenomena in 2D centrosymmetric semiconductors.

5. Experimental Section

Synthesis of MnO_2 Nanoflowers: The hierarchical MnO_2 nanoflowers were synthesized using a typical hydrothermal method with a molar ratio ($n(KMnO_4):n(KCI) = 3:1$). First, 0.4741 g KMnO_4 and 0.0746 g KCI were dissolved in 40 mL deionized water. The mixed aqueous solution was stirring continuously for 10 min at room temperature. Then the prepared precursor was transferred into the Teflon-lined stainless-steel autoclave (100 mL) and heated to 180 °C for 13 h. Finally, the nanoflowers were collected by centrifugation, and then washed and dried. All the chemical reagents were of analytical purity and used without any pre-treatment.

Materials Characterization: X-ray powder diffraction (XRD, Xpert3 Powder) with Cu K α radiation was used to characterize the

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crystallized structure of $\rm MnO_2$ nanoflowers. The microscopic features and morphologies of samples were characterized by field-emission scanning electron microscopy (SEM, Hitachi, SU8020) and HRTEM (JEM-F200).

Flexocatalysis Characterization: The MB, RhB, and MO (Aladdin Chemical Co., Ltd., Shanghai, China) dyes were used as target pollutant to evaluate the degradation activities of MnO2 nanoflowers catalysts. In this work, MnO₂ nanoflowers with various amounts (1-50 mg) were added to 50 mL dye solution (MB/RhB/MO, 10 mg L-1). Then the mixed solution was put into an ultrasonic generator (KQ-800 KDE) for catalytic degradation. All the catalytic degradation experiments were conducted in dark environment and kept at room temperature by the circulating cooling system. The ultrasonic power could be precisely set from 320 to 800 W. The temperature could be controlled by the heating function of the ultrasonic generator and the circulating cooling system. At every 30 min interval, 3 mL of the reaction solution was collected and separated from the catalyst by centrifugation (11 000 rpm, 10 min) for the determination of residual pollutant concentration. The absorption spectra of supernatant obtained by centrifuging were characterized by UV-vis spectrophotometer (UV-3600, Shimadzu, Kyoto, Japan) to determine the concentration of the target dye.

Theoretical Simulations of the Strain Distribution and Flexoelectric Polarization Distribution in Two-Dimensional Semiconductor: A cantileverbeam structure was used here to illustrate the flexoelectric effect in 2D centrosymmetric materials using COMSOL Multiphysics version 3.5. A uniform force of 100 nN was applied at the free end of the cantileverbeam while the bottom was fixed. The size of the cantilever was set to be $100 \times 20 \times 10$ nm³.

The flexoelectric polarization could be considered as a linear response to strain gradient for the cantilever-beam structure. When the force was applied in out-of-plane direction, the flexoelectric polarization could be given by:^[39]

$$P = \mu_{1122} \left(\frac{\partial u_{11}}{\partial x_3} \right) \tag{5}$$

where *P* was the polarization, μ_{1122} was the flexoelectric coefficient, and $(\partial u_{11})/(\partial x_3)$ was the strain gradient. In the calculation, the following were set: Young's modulus *E* = 200 GPa, the Poisson's ratio v = 0.2, and the flexoelectric coefficient $\mu_{1122} = 0.4$ nC m⁻¹. It should be noted that the flexoelectric coefficient were not known with certainty due to the difficulty of extracting the coefficient from the experiment, and orders-of-magnitude discrepancies may exist between experiment (much more higher) and theory for a variety of reasons.^[40–42]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

T.W. and K.L. contributed equally to this work. L.F.W. conceived the project. L.F.W., Y.Q., and T.W. designed the experiments. T.W., K.L., and

L.F.W. performed the experiments. L.F.W., Y.Q., Z.L.W., T.W., and K.L. analyzed the results. All authors contributed to discussions and writing of the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

flexoelectricity, mechanocatalysis, piezocatalysis, polarization, two-dimensional materials

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