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Boosting of water splitting using the chemical energy simultaneously harvested from light, kinetic energy and electrical energy using N doped 4H-SiC nanohole arrays[☆]

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ABSTRACT

Piezoelectric polarization promoted photoelectrochemical (PE-PEC) water splitting is a promising strategy to obtain hydrogen energy by converting light, kinetic, and electrical energy into chemical energy. However, novel piezoelectric semiconductors are urgently needed owing to the improper band positions and poor stability of most current piezoelectric materials. In this work, a method of inducing piezopotential in N doped 4H-SiC nanohole arrays (NHAs) for water splitting is proposed. The modulation effects of N doping with various contents on the electronic structure and piezoelectricity of 4H-SiC are comprehensively analyzed. By introducing piezoelectric field to regulate transport behavior of charges, the current density of NHAs reaches 6.50 mA cm⁻ at 1.4 $V_{Ag/AgCl}$, indicating a 50.1% enhancement compared with that without polarization (4.33 mA cm⁻² at 1.4 VAg/AgCl). The conjunction mechanism of photoelectric catalytic capacity and piezoelectricity of N doped 4H-SiC NHAs is elaborated, providing powerful guidance for manufacturing piezoelectric semiconductor photoanodes in PE-PEC water splitting.

1. Introduction

In the past few decades, many researchers have been working on the development of energy conversion systems and eco-friendly sustainable energy storage for combating climate change, global energy crisis, and environmental pollution [1-3]. Hydrogen (H₂) is a kind of environmentally friendly resource with a high energy density, and it has been widely considered to be the most potential clean energy [4]. H₂ production by splitting water has been a prevalent research field for obtaining green energy in recent years. The methods of splitting water including electrolysis, photolysis, photoelectrolysis, plasmolysis, magnetolysis, radiolysis and pyrolysis are widely explored [5]. Among them,

photocatalytic and photoelectrochemical (PEC) water splitting, the solar energy conversion methods of great potential, have been rapidly developed owing to the low energy consumption and environmental friendliness [6]. However, since photocatalysis can only use light energy to split water, its low efficiency of H₂ production is difficult to achieve in practical application [7]. PEC, which promotes the separation of photogenerated electron-hole pairs by introducing electricity (synergic effect of light and electrical energy), has been developed to improve H₂ production efficiency [8,9]. PEC has further advanced the low energy consumption H₂ production by splitting water, but its unsatisfactory efficiency is still the obstacle to preventing its application [10]. Considering the synergy effect between light and electrical energy, it is

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possible to design a synergic effect of multi-energy, which can further enhance the catalytic H_2 production performance by splitting water in theory.

Besides light and electrical energy, kinetic energy is also everywhere in our life as an abundant resource, such as wind blowing, water flowing, machine running, etc. Recently, the establishment of the strain-induced piezoelectric field by vibration in piezocatalysts has been proved to be capable of separating and migrating the photogenerated electron-hole pairs [11,12]. Hence, piezoelectric polarization promoted photoelectrochemical (PE-PEC) water splitting based on piezoelectric semiconductors, a strategy to directly construct piezopotential in photocatalytic semiconductors (synergic effect of light, kinetic, and electrical energy), has been considered to be the most efficient and convenient method for H₂ production [10]. To date, great attempts have been devoted to employing piezoelectric semiconductors for PE-PEC water splitting to improve H₂ production efficiency. For example, Chen et al. synthesized ZnO-WO_{3-x} nanorod arrays and applied them to PE-PEC water splitting. The optimized structure (Zn-W-5) showed a photocurrent of 3.38 mA cm⁻² at 1.23 V_{RHE} , which was 1.41 times higher than that in PEC systems [13]. Zhao et al. reported the photocurrent density of WO3/CdS can be enhanced by applying ultrasound and the maximum reached 2.13 mA cm⁻² at 1.23 V_{RHF}, which was 1.61 times before ultrasound [14]. And NaNbO₃ nanostructures prepared by Singh et al. achieved the enhancement in the photocurrent density from 0.78 mA cm⁻² to 1.02 mA cm⁻² at 1.2 $V_{Ag/AgCl}$, showing 30.8% enhancement approximately [15]. Therefore, introducing piezopotential in piezoelectric semiconductors to improve the PEC water splitting efficiency is feasible. The piezoelectric semiconductors are required to possess ideal band positions straddling the water redox potentials, moderate band gap and significant piezoelectricity [1,4]. Nevertheless, piezoelectric semiconductors commonly used in PE-PEC water splitting still suffer from deficiencies. Sulfides such as ZnS and MoS2 display improper band positions versus water redox potentials, limiting their application in overall solar water splitting [4,16]. ZnO exhibits the critical drawback of photocorrosion, resulting in unsatisfactory service life [17]. Therefore, the exploration of piezoelectric semiconductors with totally excellent PE-PEC water splitting performance is still a great challenge. In this case, 4H-SiC, one of the most important polytypism of SiC, possesses suitable band structure, excellent piezoelectricity and high physical/chemical stability, and has been a candidate in PE-PEC water splitting [8,18,19].

Herein, the strategy to induce polarization in N doped 4H-SiC nanohole arrays (NHAs) for efficient water splitting is proposed and investigated. The water splitting performance of the NHAs is enhanced by 50.1% under piezopotential. N doping is demonstrated to optimize the electronic structure and enhance piezoelectricity of 4H-SiC by first principles calculation. The conjunction mechanism of tri-harvesting light, kinetic, and electrical energy for efficient water splitting using N doped 4H-SiC NHAs is illustrated. The strain-induced piezoelectric field is proven to realize the separation and migration of electron-hole pairs, which is of great significance for the improvement of water splitting performance.

2. Experimental section

2.1. Calculation section

The first principles calculations are performed using the Cambridge Serial Total Energy Package (CASTEP) program code based on the planewave pseudo-potential method within the framework of density functional theory (DFT). The generalized gradient approximation (GGA) is adopted along with the exchange-correlation function realized by Perdow–Burke–Emzerhof (PBE). The 64-atom supercell is constructed from the conventional unit cell of 4H-SiC with $2 \times 2 \times 2$ replication. N doped 4H-SiC is modeled by introducing an N atom substituted at the central C site. The cut-off energy of 450 eV and Monkhorst–Pack grid of 10×10 \times 3 are set in this work. In FEM simulation, the size of simulated models was 1000 nm \times 1000 nm \times 60 nm. The diameter of nanoholes in NHAs was set to be 70 nm and the etching depth was 30 nm. A force of 1 mN was applied to the top surface of N doped 4H-SiC.

2.2. Materials

N doped 4H-SiC single-crystalline wafer was commercially available and cut into small sheets of 5 \times 10 mm². Acetone, ethanol (C₂H₅OH, 99%), and hydrogen peroxide (H₂O₂, 30%), were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd in China. Hydrofluoric acid (HF, 40%) and Sodium sulfate (Na₂SO₄) were from Aladdin in Beijing of China.

2.3. Fabrication of N doped 4H-SiC NHAs

N doped 4H-SiC single-crystalline sheets were ultrasonic cleaned and soaked into a solution with the volume ratio of HF to C₂H₅OH to 1:1 for 2 min to eliminate oxides. In the typical procedure, N doped 4H-SiC sheet and graphite wafer was employed as anode and cathode. The electrolyte was composed of HF: C2H5OH: H2O2 with a volume ratio of 6:6:1. Firstly, the applied pulsed voltage was 19 V with a cycle time (*T*) of 8 ms and a pause time (T_{off}) of 4 ms for a duration time of 50 s to form the cap layer. Subsequently, the silicon face of N doped 4H-SiC sheet was placed to contact the platinum electrode and a DC voltage with 21 V was utilized to detach the cap layer naturally for another 30 s. The cap layer was completely pushed apart by the gas (CO and CO₂) generated during the etching process by changing the anodic oxidation conditions [20]. Finally, the pulsed voltage was applied to tailor the growth of N doped 4H-SiC nanoarrays (NAs) for various times of 1, 5, 10, 15, and 20 min, which were denoted as samples of S1, S5, S10, S15, and S20. It should be pointed out that the openness of the resulting NAs is greatly improved by removing the cap layer, which is favorable for the occurrence of redox reactions.

2.4. Characterization

Field emission scanning electron microscope (FESEM; JSM-6701 F, JEOL, Japan) with the equipment of energy-dispersive X-ray spectroscopy (EDS; NS7, Thermo, America), X-ray diffraction (XRD; SmartLab/ Ultima IV, Rigaku, Japan), and high-resolution transmission electron microscope (HRTEM; JEM-2100, JEOL, Japan) were used for characterizations of the as-resulted N doped 4H-SiC NHAs. Their chemical states and phase composition were analyzed by Raman spectrometer (Raman; LabRAM HR Evolution, HORIBA, Japan) with an excitation laser of 532 nm. The surface species and chemical states were measured by X-ray photoelectron spectroscopy (XPS; ESCALAB 250Xi, Thermo Fisher Scientific, America). The absorption measurements were performed on a UV-vis scanning spectrophotometer (UV-3600; Shimadzu, Japan). The radical signals were detected by Electron spin resonance (ESR; A300-10/12, Bruker, Germany). The dielectric properties were recorded by the precision impedance analyzer (4294 A, Agilent, America). The piezoelectric response signals of N doped 4H-SiC NHAs were recorded by the piezoresponse force microscope (PFM; Dimension Icon, Bruker, Germany).

2.5. Photoelectrochemical (PEC) and piezoelectric-photoelectrochemical (PE-PEC) water splitting measurement

The PEC measurements of the N doped 4H-SiC NHAs were performed in a typical three-electrode configuration with a platinum counter electrode and an Ag/AgCl reference electrode in 1 M Na₂SO₄ aqueous solution, using CHI 760E electrochemical workstation. A 300 W Xe lamp with an AM1.5 filter was used in this work and the illumination intensity near the photoelectrode facade was almost 100 mW cm⁻². Mott– Schottky plots were obtained from electrochemical impedance spectroscopy at frequencies of 1000, 2000, and 3000 Hz, respectively. Linear sweep voltammetry (LSV) was carried out with a scan rate of 10 mV s⁻¹. The electrochemical impedance spectroscopy (EIS) was measured by AC impedance spectrum under a frequency that ranged from 1 to 10^5 Hz with an amplitude of the voltage of 5 mV. The amperometric I–t curves were measured with an applied potential of 1.4 V_{Ag/AgCl}. On this basis, the PE-PEC abilities N doped 4H-SiC NHAs were measured with the above PEC system by adding ultrasonic apparatus as the trigger for piezopotential.

3. Results and discussion

3.1. Effects of N doping on the electronic properties and piezoelectricity of 4H-SiC

In PE-PEC water splitting system, the piezoelectric semiconductor photoelectrode should possess a suitable bandstructure and significant piezoelectricity simultaneously [4,6]. It is well known that doping plays a vital role in tuning the electronic properties and piezoelectricity of semiconductors [21,22]. And N element is usually utilized as a doping impurity of SiC to build an n-type semiconductor [9]. Hence, the electronic structure, charge distribution and piezoelectric performance of N doped 4H-SiC were investigated.

The calculated results of 4H-SiC_{1-x}N_x demonstrate that N doping can effectively tune the band structure of 4H-SiC (Fig. 1a). The band gap of intrinsic 4H-SiC (x = 0) has been calculated to be 2.225 eV, which is much less than 3.26 eV. The error between the theoretical value and the experimental value comes from the underestimation of the correlation interaction between excited electrons in the calculation model [23]. The VBM and CBM points of intrinsic 4H-SiC are located at the M and Γ

points, indicating the indirect band gap characteristics. With the introduction of N atoms, a transition from indirect (M- Γ) to direct (Γ - Γ) band gap occurs when x = 1/64 [21,24]. And the band gap of 4H-SiC narrows down with the increase of N doping concentration, i.e., the band gap is 2.225, 2.152, 2.009 and 1.416 eV when x = 0, 1/100, 1/64 and 1/32, respectively (Fig. 1b). The indirect-to-direct transition and the narrower band gap imply the optimized optical absorption of 4H-SiC, which is beneficial for the PEC water splitting performance. In addition, once the N dopants are incorporated in 4H-SiC crystal, the remaining electrons derived from the substitution of N atoms for C atoms in 4H-SiC lattice tend to become free electrons near the bottom of the conductive band [25]. Consequently, the Fermi level enters the conduction band, indicating the typical feature of n-type doping. As the content of N doping increases, the Fermi level enters the conduction band deeper. There are some unfilled impurity energy levels near the Fermi level, which is conducive to the electronic intra-band and inter-band transitions from the occupied bands to the unoccupied bands under irradiation [23].

To accurately define the effect of N doping on the electron concentration of 4H-SiC, the electron effective mass (m_0) of 4H-SiC_{1-x}N_x was calculated (Fig. 1c). The m_0 overall shows a decreasing trend with the increase of N doping concentration, indicating the increase of electron concentration. The m_0 value of 4 H-SiC_{99/100}N_{1/100} is the highest, which can be attributed to the carrier transport in a certain direction being restricted by the enhanced anisotropy of the oversized unit cell. The carrier diffusion speed almost reaches an equilibrium when x = 1/32. Hence, 4H-SiC_{31/32}N_{1/32} was chosen to explore the effect of N doping on the charge distribution of 4H-SiC. The two-dimensional (2D) charge density plot for the (110) plane of 4H-SiC_{31/32}N_{1/32} is shown in Fig. 1d. The charge density at the N site is significantly larger than that at the C sites, demonstrating that N doping enhances the electron concentration



Fig. 1. Electronic structures of $4\text{H-SiC}_{1-x}N_x$. (a) The band structures of $4\text{H-SiC}_{1-x}N_x$. The tendency of (b) the band gap and (c) the electron effective mass of $4\text{H-SiC}_{1-x}N_x$ with increasing N doping concentration. (d) The 2D charge density plot for the (110) plane of $4\text{H-SiC}_{31/32}N_{1/32}$. The yellow color represents zero electron density while bright blue is the highest electron density. (e) The 3D charge density difference (CDD) of $4\text{H-SiC}_{31/32}N_{1/32}$. The yellow and blue represent charge accumulation and depletion respectively. (f) The corresponding 2D CDD of (001) plane. The red and blue regions represent charge accumulation and depletion.

of 4H-SiC effectively [26]. Further, a three-dimensional (3D) charge density difference (CDD) map of 4H-SiC_{31/32}N_{1/32} was investigated to verify that N doping has a significant effect on the state of charge of 4 H-SiC (Fig. 1e). The corresponding 2D counterparts of (001) plane discloses that more electrons are attracted to the side of the N-Si bond close to the N atom due to the stronger electronegativity of the N element (Fig. 1f).

To achieve extraordinary piezoelectric polarization enhancement in PEC water splitting, the piezoelectricity of 4H-SiC_{1-x}N_x was studied by first principles [27,28]. Compared with the intrinsic 4H-SiC, the N doped 4H-SiC exhibits higher values of e_{33} , indicating N doping can enhance the piezoelectricity of 4H-SiC significantly (Fig. 2a). Among them, 4H-SiC_{31/32}N_{1/32} was proved to exhibit the largest value of e_{33} of 1.36 C m⁻², which is 11.3 times that of pure 4H-SiC (0.12 C m⁻²). Therefore, 4H-SiC_{31/32}N_{1/32} was selected to analyze the enhancement mechanism of N doping on the piezoelectricity of 4H-SiC. 4H-SiC exhibits a wurtzite structure and belongs to hexagonal *P6*₃*mc* space-group symmetry, which is absent of mirror planes perpendicular to the c-axis [29]. The tetrahedral unit of 4H-SiC is composed of one C atom and four Si atoms coordinated with the C atom. According to the different chemical environments of C atoms in the tetrahedron, they are divided into two categories and denoted as C1 and C2, respectively (Fig. 2b, c). The Si-C tetrahedron of 4H-SiC is not perfect due to the different bond

lengths of Si-C bonds. Especially for the tetrahedron centered on C2 in the blue frame, the apical bond length of Si-C is 1.897 Å yet the basal one is 1.886 Å. The three Si atoms in the base plane can still be used as vertices to form an equilateral triangle. As for 4H-SiC_{31/32}N_{1/32}, the bond lengths of the tetrahedral unit centered on the N atom are all increased (Fig. 2e, f), resulting from the weaker Si-N bond due to fewer electrons being involved in forming the covalent bond of Si-N. The substitution of N atoms for C atoms will not only causes structural deformation of the single tetrahedron centered on N, but also leads to local distortions in adjacent regions. The difference between the apical bond length and the basal one of the tetrahedron centered on C2 marked in the blue frame of 4H-SiC_{31/32}N_{1/32} increases. Particularly, the three Si atoms on the base plane occupy different coordinates along C axis, confirming the notable tetrahedron distortion. The lattice constant marked in (001) planes of 4H-SiC and 4H-SiC $_{31/32}N_{1/32}$ further proves that N doping makes the crystal structure more asymmetric (Fig. 2d, g). Hence, 4H-SiC_{31/32}N_{1/32} possesses greater local structural heterogeneity than 4H-SiC, resulting in higher piezoelectricity [30]. In addition, the distance between the positive and negative charge centers in the tetrahedral unit determines the strength of the dipole of 4H-SiC, which in turn affects piezoelectricity. Taking C2 tetrahedrons marked in blue frames as examples, the dipole moments before and after N doping are 10.19 Com and 10.51 Com approximately, demonstrating the



Fig. 2. Piezoelectric performance of $4\text{H-SiC}_{1-x}N_x$. (a) The tendency of the value of e_{33} of $4\text{H-SiC}_{1-x}N_x$ with increasing N doping concentration. (b) The crystal structure, (c) C1 and C2 tetrahedrons and (d) the crystal structure of (001) planes of 4H-SiC. (e) The crystal structure, (f) C1 and C2 tetrahedrons and (g) the crystal structure of (001) planes of $4\text{H-SiC}_{31/32}N_{1/32}$. (h) Geometry schematic and (i) the distribution of calculated piezopotential of $4\text{H-SiC}_{31/32}N_{1/32}$ bulk. (j) Geometry schematic and (k) the distribution of calculated piezopotential of $4\text{H-SiC}_{31/32}N_{1/32}$.

strengthening effect of N doping on the piezoelectricity of 4H-SiC. Overall, x = 1/32 is the best doping concentration to comprehensively improve the photoelectric and piezoelectric performance of 4H-SiC.

In addition to composition, the morphology of 4H-SiC also plays a key role in PE-PEC water splitting. On one hand, the morphology of the photoelectrode materials affects the specific surface area, the charge separation efficiency and light absorption capacity, playing an important role in determining the PEC performance. The photoelectrode with 3D nanostructure has a complex geometric morphology, a larger surface area and better charge transfer properties compared to the lower dimensional structures, which has become the optimal choice for satisfying efficiency [31]. On the other hand, the morphology also influences the piezoelectric response of N doped 4H-SiC under the same external force. For example, N doped 4H-SiC NHAs were chosen to be compared with bulk on macroscopic piezoelectric behavior by finite element method (FEM) simulations here (Fig. 2h, j) [32]. The calculated maximum negative piezopotential generated from bulk and NHAs is - 1.56 V and - 2.03 V, indicating that the piezoelectric performance of N doped 4H-SiC NHAs is better than the bulk (Fig. 2i, k). Therefore, NAs, especially 3D NHAs, are more suitable to obtain the best PE-PEC water splitting performance.

Overall, N doped 4H-SiC was confirmed to possess a narrower band gap, higher carrier concentration and better piezoelectricity than intrinsic 4H-SiC. Especially, the 4H-SiC_{31/32}N_{1/32} exhibits an ideal electron concentration and the highest value of e_{33} . Hence, N doped 4H-SiC (4H-SiC_{31/32}N_{1/32}) NAs will be selected for subsequent experimental tests.

3.2. Preparation and characterization of N doped 4H-SiC NAs

The schematic illustration of the fabrication of N doped 4H-SiC NHAs is shown in Fig. 3a [20,33]. The morphologies of the N doped 4H-SiC bulk sheet and NAs fabricated by anodic oxidation for 1, 5, 10, 15, and 20 min (S1, S5, S10, S15, and S20) were characterized by scanning electron microscope (SEM) (Fig. 3b-g). The top view of the N doped 4H-SiC bulk sheet and the cap layer were shown in Fig. 3b. The cap layer was removed to enhance the openness of the NHAs, allowing more catalytic active sites to be generated and exposed. In addition, the fully open nanohole channel makes the electrolyte flow in easily, thereby increasing the contact area between the catalytic site and the electrolyte and facilitating water splitting [33-35]. After removing the cap layer, extremely small holes are distributed evenly on the surface of N doped 4H-SiC when the etching time is 1 min (Fig. 3c). With the extension of etching time, the pore size of nanohole increases and the sidewalls are gradually penetrated. As a result, the NAs transform from NHAs to nanobelt arrays (NBAs) within 20 min (Fig. 3d-g). Sample S10 was ground and characterized by the transmission electron microscope (TEM) (Fig. 3h). The special bamboo-like shape structure comes from the voltage oscillation, the applied pulsed voltage and the different etching rates of between carbon and silicon surfaces [18,35]. The interplanar spacing in high-resolution TEM (HRTEM) images was measured to be 0.251 nm (Fig. 3i), corresponding to the (004) face of 4H-SiC. The select area electron diffraction (SAED) patterns were obtained by fast Fourier transform (FFT) of HRTEM image and verified to be consistent with 4H-SiC. XRD patterns of 4H-SiC bulk sheet, sample S10 and the powder of sample S10 are displayed in Fig. 3j. All the peaks of the powder of sample S10 are well matched with standard cards of



Fig. 3. Morphology, crystal structure and chemical states of N doped 4H-SiC NAs. (a) Schematic illustration of the fabrication of N doped 4H-SiC NHAs. (b-g) SEM images of 4H-SiC bulk sheet and samples of S1, S5, S10, S15, and S20. The illustration in the lower left corner in b is the SEM image of the cap layer. (h) Low-magnification TEM image of sample S10. (i) HRTEM image and corresponding SAED of sample S10 recorded from the marked area A in panel (h). (j) XRD patterns of sample S10, 4H-SiC bulk sheet and the powder of sample S10. (k) The high-resolution XPS spectra of N 1 s of sample S10.

4H-SiC (JCPDS Card No. 73–1664). The sharp peaks of sample S10 and bulk sheet at 35.6° agree well with the (004) crystal plane of 4H-SiC, indicating their high crystallinity with a single-crystalline structure. Furthermore, the Raman spectra of samples S1-S20 also accurately display the characteristics of 4H-SiC (Fig. S1) [9]. The full XPS spectrum reveals the co-existence of C, Si, O, and N in sample S10 (Fig. S2a). The fine XPS spectra of C 1 s, Si 2p and O 1 s were illustrated in Fig. S2b-d. The N 1 s spectrum in Fig. 3k confirms that the N dopants are incorporated within 4H-SiC. And the N doping content of 4H-SiC is calculated to be 1.37 atom %, which is close to 4H-SiC $_{31/32}N_{1/32}$. The typical energy dispersive spectroscopy (EDS) mappings confirm that N atoms are evenly distributed in 4H-SiC (Fig. S3).

The atomic force microscope (AFM) topographic images of N doped 4H-SiC bulk sheet and sample S10 in the range of $5 \times 5 \ \mu m^2$ are presented in the upper and lower panels of Fig. 4a, respectively. Compared with the bulk sheet, sample S10 exhibits a rougher surface due to the anodic oxidation. The UV–Vis diffuse reflectance spectra (DRS) and corresponding Tauc plots of pure and N doped 4H-SiC are disclosed in Fig. S4, proving that N doping in 4 H-SiC can efficiently narrow the band gap and improve light absorption, which is beneficial to the PEC/PE-PEC water splitting performance [22]. Compared with the N doped 4H-SiC bulk sheet, the nanostructures formed by anodic oxidation are

beneficial to enhance the optical absorption capacity (Fig. S5). The N doped 4H-SiC with the nanohole structure (sample S10) exhibits better light absorption capacity among all the samples, verifying the potential advantage of this 3D nanostructure in PEC catalytic performance [31]. Particularly, the optical band gap of sample S10 is calculated to be 2.94 eV (Fig. 4b). Mott-Schottky measurements were performed to further investigate the band structure of sample S10 (Fig. 4c). The positive slope of C^{-2} versus V shows the behavior of a typical n-type semiconductor in nature. The position of the flat band potential $(E_{\rm fb})$ for sample S10 is estimated to be - 0.92 $V_{\mbox{Ag/AgCl}}.$ And the conduction band minimum (CBM) and the valence band maximum (VBM) are determined as $-0.42 V_{RHE}$ and 2.52 V_{RHE} , respectively, where RHE is the abbreviation of reversible hydrogen electrode [9]. Therefore, the energy band positions of sample S10 straddle the water redox potentials ideally [4]. The electron spin resonance (ESR) results of sample S10 indicate that active species including $\bullet OH$, $\bullet O_2$ and 1O_2 were generated under illumination for 30, 60 and 120 s (Fig. 4d-f), fully demonstrating the outstanding light absorption capacity.

The dielectric constant and dielectric loss of pure and N doped 4H-SiC bulk as a function of frequency were measured and plotted in Fig. S6. In the lower frequency range, the dielectric constant and loss exhibit relatively high values, resulting from the more active



Fig. 4. Optical properties, radical signals and piezoelectric response of sample S10. (a) AFM topographic images of bulk sheet (top) and sample S10 (bottom). (b) UV–Vis DRS of sample S10. The inset is the corresponding Tauc plot. (c) Mott–Schottky plots obtained from electrochemical impedance spectroscopy at frequencies of 1000, 2000, and 3000 Hz. ESR results of sample S10 under illumination for 30, 60, and 120 s: (d) \bullet OH, (e) \bullet O₂, and (f) ¹O₂. Piezoresponse amplitude loop with butterfly-shaped hysteresis curves of (g) bulk sheet and (h) sample S10. (i) ESR signals for \bullet OH of sample S10 in dark with and without vibration operation.

polarizations. As the frequency increases, dipoles have such difficulty changing orientation with the rapidly oscillating electric field that the permittivity and the loss decrease until remain almost constant [36,37]. Notably, the dielectric constant of N doped 4H-SiC is significantly increased compared to that of pure 4H-SiC, indicating that N doping is capable of regulating the dielectric properties effectively. Further, the butterfly-shaped hysteresis loops of N doped 4H-SiC bulk sheet and the sample S10 illustrate that the NHAs possess more pronounced piezoelectric responses than the bulk (Fig. 4g, h), which is consistent with the FEM simulation results. To verify the effect of piezoelectricity on water splitting, the signal of •OH was detected after sample S10 underwent an ultrasonic operation for 5 min in dark, verifying that abundant charges are generated to produce reactive species (Fig. 4i) [38]. The amplitude of polarization in N doped 4H-SiC decreases and increases periodically under periodical stress, leading to the continuous redistribution of bound and screening charges. During this process, continuous free charges are generated to participate in the redox reaction and produce •OH [38.39].

3.3. PEC and PE-PEC water splitting performance of N doped 4H-SiC NHAs

As a comparison, the water splitting performance of pure and N doped 4H-SiC bulk in dark and under illumination were explored (Fig. S7). N doped 4H-SiC bulk shows a current density of 0.50 mA cm⁻² under illumination, which is superior to the pure one due to the narrower band gap and higher carrier concentration. To achieve higher water splitting efficiency, N doped 4H-SiC NAs with various morphologies were fabricated and utilized as photoanodes for PEC water splitting (Fig. 5a). Remarkably, the water splitting activity of N doped 4H-SiC is significantly enhanced by the construction of nanostructure arrays. The current density of the samples of S1, S5, S10, S15, and S20 under illumination is 3.20, 3.70, 4.33, 3.43, and 2.57 mA cm⁻² at 1.4 V_{Ag/AgCl}, of which sample S10 exhibits the highest photocurrent density. The current density of sample S10 achieves 0.54, 2.49, 4.33, and 9.26 mA cm⁻² when in dark and under illumination with light intensities of 50, 100, and 200 mW cm⁻² (Fig. S8). With the increase of



Fig. 5. PEC and PE-PEC water splitting performance of N doped 4H-SiC NAs. (a) LSV and (b) EIS curves of N doped 4H-SiC bulk sheet and the samples of S1, S5, S10, S15, and S20 under illumination. The inset is the fitted simplified equivalent circuit. (c) LSV curves of sample S10 in dark, under illumination and illumination with ultrasonic vibration. (d) LSV curves of N doped 4H-SiC NHAs (sample S10) under illumination with different ultrasonic vibration power. (e) I–t curves of N doped 4H-SiC NHAs (sample S10) under illumination with different powers. (f) Schematic illustration of simultaneously harvesting diversified energies for water splitting using N doped 4H-SiC NHAs. i. Kinetic/electrical energy. ii. Light/electrical energy. iii. Light/kinetic/electrical energy. The white line represents the initial band edge. The green line represents the band edge under electric field. The red line represents the band edge under electric and piezoelectric fields. (g) I–t curves of N doped 4H-SiC NHAs (sample S10) at 1.4 V_{Ag/AgCl} under chopped simulated sunlight and illumination with on-off ultrasonic vibration.

light intensity, more photogenerated carriers are generated and participate in the redox reactions, resulting in a higher current density. Subsequently, electrochemical impedance spectroscopy (EIS) was measured to investigate the charge transfer characteristics of N doped 4H-SiC NAs. The smaller the arc radius of the Nyquist plot, the lower the charge transfer resistance. Sample S10 shows the lowest charge transfer resistance (Fig. 5b), and the details are displayed in Table S1. Compared with the N doped 4H-SiC bulk sheet, the NAs show a better PEC water splitting performance [40]. Firstly, the establishment of nanostructure provides a larger surface area, increasing the photoanode/electrolyte interface area and benefitting water splitting. Secondly, the N doped 4H-SiC NAs exhibit abundant light absorption paths, improving the light absorption efficiency. Thirdly, the carrier separation and collection efficiency of the NAs are significantly enhanced by reducing the distance that minority carriers must travel. Hence, the N doped 4H-SiC NAs fabricated by anodic oxidation will show a better water splitting performance. Further, the N doped 4H-SiC NHAs (sample S10) show the best PEC water splitting capability among all of the samples. At the beginning of anodic oxidation, the smaller nanohole appears. Yet the smaller nanohole has only a limited surface area, resulting in unsatisfactory performance. As the etching time increases, the nanohole in arrays gets bigger and bigger until the sidewalls are penetrated to form the nanobelt. Finally, the morphologies of NAs transform small nanoholes and big nanoholes into nanobelts. Compared with the lower dimensional nanobelts, the 3D nanohole has a complex geometric morphology with a richer surface area and better charge transfer properties [8,31]. Therefore, the N doped 4H-SiC NHAs shows the best water splitting performance among all the samples and will be applied to the following PE-PEC water splitting tests.

In PE-PEC water splitting, the N doped 4H-SiC NHAs were used to harvest light, kinetic, and electrical energy simultaneously. The NHAs exhibit negligible current density (0.54 mA cm⁻² at 1.4 V_{Ag/AgCl}) in dark and shows a distinct improvement under illumination (4.33 mÅ cm⁻² at 1.4 VAg/AgCl) (Fig. 5c). Vast photogenerated carriers generated inside N doped 4H-SiC participate in the redox reaction, improving the water splitting performance significantly. Under simulated solar light irradiation with 120 W ultrasonic vibrations, the current density of N doped 4H-SiC NHAs reaches up to 6.50 mA cm^{-2} at 1.4 $V_{\text{Ag/AgCl}}$, which is an increase of 50.1% compared with that under illumination without vibration (Fig. 5c). Subsequently, the photocurrent density of N doped 4H-SiC NHAs was measured under ultrasonic vibrations with different power to define the effect of piezoelectric field on PEC water splitting activity. The photocurrent density increases as the power of ultrasonic vibration rises (Fig. 5d). Specifically, the photocurrent density of the NHAs under ultrasonic vibration of 24, 48, 72, 96, 120 W is 4.67, 5.00, 5.30, 5.90, 6.50 mA $\rm cm^{-2}$ at 1.4 $\rm V_{Ag/AgCl}$, which is increased by 7.9%, 15.5%, 22.4%, 36.3%, and 50.1%, respectively. The enhancement of current density is insignificant compared with the enhancement of the e_{33} values, which can be attributed to the strategy of PE-PEC water splitting is mainly focused on improving the transport behavior of electrons and holes both in bulk and on the surface of N doped 4 H-SiC rather than the whole PEC process [10].

To eliminate the effect of increased mass transfer and the removal of bubbles, N doped 4H-SiC NHAs were measured under various conditions, i.e. in dark, in dark with stirring, and in dark with ultrasonic vibration (Fig. S9). The current density of NHAs in dark with and without stirring is almost the same, indicating that the enhanced mass transfer and the elimination of bubbles are not the key points [12]. Notably, the PEC water splitting activity of N doped 4H-SiC NHAs in dark with ultrasonic vibration is significantly enhanced, proving that the piezoelectric field with uniform orientation in the single crystalline NHAs plays a dominant role.

The transient piezo-current density curves measured at $1.4 V_{Ag/AgCl}$ indicate that N doped 4H-SiC NHAs are pretty sensitive to the switch of ultrasonic vibrations in dark (Fig. 5e). The NHAs show a quite low current density in dark, while a distinct enhancement appears once the

ultrasonic vibration is applied. And the strengthening effect tends to be more remarkable as the ultrasonic vibration power increases. The bubbles generated by ultrasonic vibration burst quickly, resulting in a local pressure even greater than 100 MPa. Under extreme pressure, N doped 4H-SiC NHAs are deformed and then internally polarized, generating a piezoelectric field and manipulating band structure (i in Fig. 5f). Firstly, band bending is adjusted by applying a potential between the working electrode and the reference electrode. When a positive bias is applied to the N doped 4H-SiC, all changes in applied bias fall on the depletion layer and make it increase, resulting in increased upward band bending in the interface between the semiconductor and electrolyte (green line) [41]. Secondly, when a tensile strain is applied simultaneously, a negative piezopotential appears at the side of N doped 4H-SiC directly interfacing with the electrolyte, leading to a further upward bending of the band edge (red line). In this case, the migration of electrons becomes easier and the local resistance or threshold voltage for surface oxidation reaction is reduced efficiently, which is favorable for enhancing the water splitting performance [10,42]. In addition to manipulating the band structure, the piezoelectric field also plays a key role in accelerating the separation and transport of carriers [7,10,43]. The significant piezoresponse of N doped 4H-SiC NHAs indicates available charges induced by the piezopotential appear on the surface to participate in redox reactions [44]. Typically, more free charges and larger piezopotential are generated under ultrasonic vibration with a higher power, leading to a prominent increment of piezocatalytic activity [43].

The collaborative effect of harvesting light, kinetic, and electrical energy simultaneously by N doped 4H-SiC NHAs in PE-PEC water splitting was further explored (Fig. 5g). The transient photocurrent density curves measured at 1.4 VAg/AgCl under chopped illumination show that the NHAs exhibit an evident light response, indicating abundant photogenerated carriers are generated rapidly within NHAs under illumination (ii in Fig. 5f). There is a sharp drop in the current density, demonstrating the nonnegligible recombination of photogenerated electron-hole pairs in PEC water splitting. A stable photocurrent density is obtained until the separation and recombination of the carriers reach a dynamic equilibrium [11]. The photocurrent density of the NHAs also exhibits a significant piezoelectric response under ultrasonic vibration, verifying the feasibility of tri-harvesting light, kinetic, and electrical energy. The coexistence of electric and piezoelectric fields makes the band edge of N doped 4H-SiC in contact with electrolyte bend sufficiently upward, while significantly suppressing the recombination of charges. Hence, the abundant free carriers generated inside SiC under illumination are fully separated and transmitted to the surface to participate in the redox reactions (iii in Fig. 5f). The larger the ultrasonic power, the greater the deformation of the NHAs, and the more remarkable the enhancement of piezoelectric effect on PEC water splitting ability. Notably, the photocurrent density under 120 W ultrasonic vibration is larger than the maximum value of that without ultrasonic vibration, fully demonstrating that continuous free charges generated in N doped 4H-SiC NHAs by piezopotential contribute to the enhancement of the PEC water splitting [11,22,38]. The durability of N doped 4H-SiC NHAs at 1.4 $V_{Ag/AgCl}$ under illumination with and without ultrasonic vibration was tested (Fig. S10). The improvement of PEC water splitting performance of the NHAs caused by piezoelectric effect is significant in 15000 s. Therefore, coupling the photoexcitation and piezoelectricity of N doped 4H-SiC NHAs to harvest light, kinetic, and electrical energy simultaneously is a promising strategy to achieve high-efficiency water splitting.

The results are also compared with the reported SiC and classic piezoelectric materials in the literature (Table 1). Synergistically harvesting light, kinetic, and electrical energy for efficient water splitting based on the N doped 4H-SiC NHAs is proposed for the first time. As a novel piezoelectric semiconductor capable of simultaneously realizing photoexcitation and piezoelectric polarization, N doped 4H-SiC NHAs are competitive in both the PEC and PE-PEC water splitting fields.

Table 1

Comparison of PEC (J^{a}) and PE-PEC (J^{b}) water splitting performance of the reported SiC and classic piezoelectric materials.

Materials		J^a (mA cm ⁻²)	J^b (mA cm ⁻²)	Ref.
SiC	3C-SiC	0.12 (1.23 V _{RHE})	_	[45]
	NiO/3C-	1.18 (1.23 V _{RHE})	-	[46]
	SiC			
	4H-SiC	3.20 (1.23 V _{RHE})	-	[9]
	4H-SiC	2.41 (1.4 V _{Ag/}	-	[8]
		AgCl)		
	Pt/3C-SiC	1.6–5.4 (1.4 V _{Ag/}	-	[47]
		AgCl)		
Piezoelectric	ZnO	0.54 (1.5 V _{SCE})	0.6 (1.5 V _{SCE})	[48]
materials	ZnO	0.27 (1.23 V _{RHE})	0.45	[11]
			(1.23 V _{RHE})	
	CdS	1.57 (1.23 V _{RHE})	3.09	[49]
			(1.23 V _{RHE})	
	Cd _{0.4} Zn _{0.6} S	~0.6 (1.23 V _{RHE})	~0.7	[44]
			(1.23 V _{RHE})	
	CdS	0.59 (1.23 V _{RHE})	0.89	[14]
			(1.23 V _{RHE})	
	KNbO ₃	\sim 0.68 $ imes$ 10 ⁻³	$0.82 imes 10^{-3}$	[50]
		(0 V _{Ag/AgCl})	(0 V _{Ag/AgCl})	
	NaNbO ₃	0.78 (1.2 V _{Ag/}	1.02 (1.2 V _{Ag/}	[15]
		AgCl)	AgCl)	
	NaNbO ₃	1.52 (1 V _{Ag/AgCl})	4.83 (1 V _{Ag/}	[51]
			AgCl)	
	MoS_2	~2.2 (1.7 V _{RHE})	~5.0	[12]
			(1.7 V _{RHE})	
N doped 4H-SiC NHAs		4.33 (1.4 V _{Ag/}	6.50 (1.4 V _{Ag/}	This
		_{AgCl})	_{AgCl})	work

4. Conclusion

In summary, the conjunction mechanism of tri-harvesting light, kinetic, and electrical energy for efficient water splitting using N doped 4H-SiC NHAs was demonstrated. 4H-SiC_{31/32}N_{1/32} was pointed out to be the optimal doping amount to obtain the best synergistic effect of photo absorption ability and piezoelectricity by first principles calculation. The NHAs reached a current density of 6.50 mA cm⁻² at 1.4 V_{Ag/AgCl} under simulated solar light irradiation and a 120 W ultrasonic vibration, which is a 50.1% improvement over the current density under illumination alone (4.33 mA cm⁻² at 1.4 V_{Ag/AgCl}). The existence of piezopotential in N doped 4H-SiC not only modulates band structure but also speeds up the separation and migration of free charges, leading to the enhancement of water splitting capability. This provides a promising approach to simultaneously harvesting diversified energies for efficient acquisition of hydrogen energy.

CRediT authorship contribution statement

Zhou Linlin: Methodology, Writing - original draft. Yang Tao: Writing – original draft, Writing - review & editing, Funding acquisition. Fang Zhi: Methodology, Investigation. Zhou Jiadong: Formal analysis. Zheng Yapeng: Investigation. Guo Chunyu: Investigation. Zhu Laipan: Data curation, Validation, Funding acquisition. Wang Enhui: Investigation, Funding acquisition. Hou Xinmei: Supervision, Project administration, Funding acquisition. Chou Kuo-Chih: Supervision, Resources. Wang Zhong Lin: Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Research data are not shared.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2022.107876.

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