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Synergistically Active Piezoelectrical H₂O₂ Production Composite Film Achieved from a Catalytically Inert PVDF–HFP Matrix and SiO₂ Fillers

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Abstract: Local and decentralized H_2O_2 production via a piezoelectrical process promises smart biological utilization as well as environmental benefits. However, stable, bio/ environmentally safe, and easily applied H_2O_2 generation materials are still lacking. Here, we report a novel flexible H_2O_2 generation polymeric film composed of catalytically inert PVDF–HFP (Poly(vinylidene fluoride-co-hexafluoropropylene)) matrix and SiO₂ nanoparticle fillers. The film is bio-/ environmentally benign at resting states, but effectively produces H_2O_2 upon ultrasonic motivation at a production rate of 492 µmolg⁻¹ in one hour. Experimental and simu-

Introduction

Hydrogen peroxide (H_2O_2) is one of the most important chemicals in modern chemical industry as well as biomedical treatment.^[1] Currently, the anthraquinone method is used in industry to produce H_2O_2 .^[2] However, novel methods to produce H_2O_2 locally are highly demanded because of the inconveniences of current H_2O_2 production and transportation strategies. Locally generating H_2O_2 piezoelectrically from ambient H_2O and/or O_2 is appealing because of the following advantages,^[3] including (i) low-level waste discharge, (ii) waiving the risk in H_2O_2 transportation or storage since H_2O_2 is highly corrosive and explosive, and (iii) energy-economic since H_2O_2 can be produced via mechanical vibrations during the process of regular ultrasonic cleaning or machine-cleaning.

A wide range of piezoelectrically active materials have been developed for locally generating H_2O_2 recently, including perovskite structured particles,^[3a,b] bismuthate particles^[3c] or sheets,^[3d] metal sheet,^[3e] engineered C_3N_4 sheets^[3f] or other heterojunctions.^[3g-i,4] The piezoelectrical fields generated within

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Department of Pain, The First Medical Center of Chinese PLA General Hospital, Beijing, 100853 (P. R. China) E-mail: beijing 301@sina.com lation methods in combination indicate that the effective H_2O_2 generation capabilities stem from the synergistic existence of piezoelectrical fields and the air-liquid-solid three-phase regions around the porous film. The chemical conversions are motivated by the adsorbed charges. The silicon hydroxyl groups properly stabilize the *OOH intermediate and facilitate the chemical conversions of $2e^-$ ORR of ambient O_2 . We expect the report to inspire H_2O_2 piezoelectrical generation materials and promote the novel production strategies of H_2O_2 as well as piezoelectrical functional materials.

these structures (i) manipulate the band structure of the semiconductor catalyst,^[5] (ii) motivate electron transitions,^[6] (iii) promote the separation and transportation of charge carriers,^[7] and (iv) generate or adsorb screen charges around the particulate structures.^[8] These factors synergistically function to realize the catalytic H_2O_2 generation, mostly via O_2 reduction pathways.

Despite these important advances in developing piezoelectrically active H_2O_2 – generating materials, urgent challenges for novel material exploration still remains for the following reasons. Firstly, H_2O_2 is widely used in biomedical scenarios,^[1c-e] such as disinfection, hemostasis, initiating neoangiogenesis, reducing ulcer area, and enhancing wound healing by improving circulation. However, bio-safe materials^[9] that piezoelectrically generate H_2O_2 are still lacking. Secondly, the developed piezoelectrically active H_2O_2 generating materials are mostly powders, which are difficult to apply or collect after use, imposing oxidizing pressure if discharged into environment. For these reasons, to develop film materials that can piezoelectrically generate H_2O_2 from ambient O_2 or H_2O from bio-safe components is highly demanding.

In this report, we devise a flexible composite polymeric film that can piezoelectrically generate H_2O_2 from bio-safe PVDF–HFP (Poly(vinylidene fluoride-co-hexafluoropropylene)) film and SiO₂ nanoparticles. Either PVDF–HFP or SiO₂ particle is inert in generating H_2O_2 . However, when compositing these two types of components using proper methods, the composite SiO₂/PVDF–HFP film is not only piezoelectrically active but is also effective in generating H_2O_2 via O_2 2e⁻ reduction process at a production rate of 492 µmol g⁻¹ h⁻¹, comparable with powderform catalysts. SiO₂ promotes the piezoelectrical capability of PVDF–HFP and at the same time serves as the adsorption site of the catalytic intermediate. PVDF–HFP provides piezoelectrical

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fields that generate or attract free charges from solution environment and enable electron translocation to initiate chemical conversions. Considering polymeric film matrix buries a large proportion of catalytic active sites in usual materials designs, the high piezoelectrical H_2O_2 productivity comparable with powder catalysts is unexpected.

This report provides a feasible strategy for producing a high-performance film-state H₂O₂ piezoelectrical generating material system. The scientific information in this report serves two perspectives. Firstly, composite films that effectively generate H₂O₂ in piezoelectrical process are developed using bio-safe building components, facilitating biomedical applications. Secondly, the study indicates that when embedding hydrophilic nanocomponent in piezoelectrically active polymer films, the film fabricated from entirely catalytically inert components can chemically convert ambient O₂ to H₂O₂ due to the synergistic function of screening charges around the materials and three-phase interface established inside the porous films. Since compositing polar nanoparticles with PVDF-HFP has been increasingly used to enhance its piezoelectrical capabilities, cautions should be taken when used in biomedical scenarios to avoid unintended oxidizing pressure for their H₂O₂ generation capabilities. For these reasons, we expect our study to inspire novel design of H₂O₂ locally generating materials, and promote appropriate applications of piezoelectrically active materials in biomedical scenarios.

Results and discussion

Characterizations of the composite film

The SiO₂/PVDF–HFP–X (X = x wt% SiO₂ in film sample) composite films are prepared by blend-casting followed by phase separation (Figure 1a). The phase separation step is realized by spraying water into the casted film with solvent DMAc, when the hydrophobic PVDF–HFP polymer is repelled by the water phase and form microporous morphologies upon drying. The pore generation step can also enhance the piezoelectricity since water droplets herein also perform as the polar templates to polarize the PVDF–HFP polymer chains to boost the piezoelectrically active β -phase fraction.^[10] The prepared porous film presents homogeneous porosity with pore diameter of around 2–5 µm, separated by pore walls with thickness of around 1 µm. And SiO₂ particles with the diameter of around 15 nm are incorporated in the porous film as fillers, shown in Figure 1b.

Upon ultrasonication at air–water interface, H_2O_2 can be produced via chemical conversion by the composite SiO₂/ PVDF–HFP films. The fractions of the SiO₂ particles (the value of X) significantly influence the productivity of H_2O_2 . When varying the fraction of SiO₂ particles between 0 and 30 wt%, the composite film with 10 wt% SiO₂ particles (SiO₂/PVDF–HFP–X) produces H_2O_2 the most effectively at a rate of 246 µmolL⁻¹ h⁻¹.

It's surprising that the composite SiO₂/PVDF–HFP–X films effectively produce H_2O_2 upon ultrasonication in EtOH aqueous solution (20 v%), since both PVDF–HFP and SiO₂ are catalytically inert and cannot produce H_2O_2 even under ultrasonication

motivations as shown in Figure 1c. In contrast, SiO₂/ PVDF-HFP-X (X between 5 and 30) films produce H₂O₂ effectively and SiO₂/PVDF-HFP-10 produce the highest amount of H₂O₂ in this series of samples with a productivity of 246 $\mu mol\,L^{-1}\,h^{-1}$ or 492 $\mu mol\,g_{SiO_2}^{-1}$ during 60 min. The catalytic ability remains even after 30 days preservation in ambient environment which proves its excellent stability. The H₂O₂ productivity is comparable to other granular catalysts and the material is easy to recover for its film feature (Figure 1d& Table S1). In addition, compared with perovskite or other semiconductor catalysts,^[11] this composite film is simply prepared from bio-safe materials and is stable upon long-term preservation in ambient environment.^[12] The H₂O₂ production capability of $SiO_2/PVDF-HFP-10$ is 24.6 times that of the pure PVDF-HFP polymer film in EtOH aqueous solution and 10 times that of SiO₂/PVDF–HFP-10 in pure water (Figure S1). The unprecedented H₂O₂ production capability of SiO₂/PVDF-HFP-10 is further studied in detail.

X-ray photoelectron spectroscopy (XPS) characterizations as shown in Figure 2(a-d) indicate intermolecular interactions between SiO₂ and PVDF-HFP. All constituent elements can be observed in XPS survey spectra (Figure 2a). While attention should be paid that the broad O 1s XPS spectrum displays an increase in binding energy of about 1.0 eV for SiO₂/PVDF-HFP-10 compared with SiO₂ particles (Figure 2b). Meanwhile, the binding energy for Si 2p decreased by 1.2 eV from 103.48 eV in SiO₂ to 102.28 eV for SiO₂/PVDF-HFP-10 (Figure 2c). These changes illustrate evidently that O atoms of SiO₂ donate electron densities to H-C in PVDF-HFP, forming intermolecular hydrogen bonds,^[13] and weakening the Si–O bond in SiO₂. In the meantime, the location of the F 1s peak keeps almost unchanged before and after compounding (Figure 2d), which implies strongly that the H-bond may be formed between Si-O and C-H. Such matrix-filler hydrogen bonds would promote the spontaneous polarization of the PVDF-HFP molecular chain for the formation of the piezoelectrically active β -phase and boost piezoelectricity.^[14]

Density functional theory (DFT) calculations further corroborate the intermolecular interactions between SiO₂ fillers and PVDF-HFP matrix. Figure S2 shows three types of possible absorption structures between SiO₂ lattice and α -PVDF, β -PVDF (H plane), and β -PVDF (F plane), respectively. The relative stability can be deduced from the adsorption energy calculation. It is found that the model with the H-plane of β -PVDF pointing toward SiO_2 (-0.66 eV) is more stable than F-plane (-0.58 eV). This means SiO₂ most likely tends to combine with PVDF via interacting with H-plane to promote β phase crystallization. In comparison, α -PVDF/SiO₂ is the most unstable structure with the highest adsorption energy (-0.44 eV). The Differential charge density analysis indicates that electrons transfer from H atoms of PVDF to O atoms of SiO₂ (Figure 2e), consistent with XPS analysis. Taken altogether, introducing SiO₂ filler is in favor of β -PVDF crystallization due to the formation of C-H-O hydrogen bond, boosting the piezoelectricity. The enhanced crystallization (β phase formation) of these samples is further investigated by X-Ray Diffraction (XRD) spectra (Figure 2f). The diffraction peak at $2\theta = 20.26^{\circ}$ corresponding to the 861471x, 2022



Figure 1. SiO₂/PVDF–HFP film design, morphology, and H_2O_2 generation performance (PS–X denotes SiO₂/PVDF–HFP–X). a) The illustrative scheme of the SiO₂/PVDF–HFP composite film and the chemical conversion process around the gas-liquid-solid three-phase area in the film. b) SEM images of SiO₂/ PVDF–HFP-10. c) Piezocatalytic H_2O_2 generation performance of the series of films with varying SiO₂ fractions. d) Comparison between this work and other piezoelectrical H_2O_2 production materials reported in recent years.

(100) (200) facets of $\beta\text{-PVDF}$ enhances relative to the peak at $2\theta\!=\!18.3^\circ$ corresponding to the (020) facet of $\alpha\text{-PVDF}$ in SiO₂/ PVDF–HFP-10 compared with the pristine PVDF–HFP.^[15]

This trend is also supported by attenuated total reflection infrared spectroscopy (ATR-IR) spectra (Figure 2g). The vibrational peaks detected at 1270, 840 cm⁻¹ correspond to β -phase, where the peaks at 971, 764 cm⁻¹ are assigned to α -phase.^[16] The β -PVDF fractions increase from 49% of the pure PVDF–HFP film to 62% of SiO₂/PVDF–HFP-10, calculated using the following formula:^[17]

$$F(\beta) = \frac{A_{\beta}}{\binom{K_{\beta}}{K_{\alpha}}A_{\alpha} + A_{\beta}}$$
(1)

where A_{β} is the absorbance at 840 cm⁻¹, and A_{α} is the absorbance at 764 cm⁻¹. K_{β} and K_{α} (7.7×10⁴, 6.1×10⁴ cm² mol⁻¹) are absorption coefficients at 840 cm⁻¹ and 764 cm⁻¹, respectively.

Fourier transform infrared (FT-IR) spectra also reveal the functional groups belonging to amorphous SiO_2 (Figure S3). The peaks at 1103, 801, and 467 cm⁻¹ present anti-symmetrical vibrations, symmetrical vibrations, and torsion vibrations of the Si–O–Si bond respectively. The peak locates at 958 cm⁻¹ is



Figure 2. The filler-matrix interaction of the SiO₂/PVDF–HFP composite film and the resultant appealing piezoelectrical performance (PS–X denotes SiO₂/PVDF–HFP–X). a) XPS spectrum Survey of samples, b) O 1s, c) Si 2p, and d) F 1s XPS spectra of samples. e) Differential charge density of SiO₂/PVDF–HFP. f) XRD spectra of the composite film as well as its building units. g) ATR-IR spectrum of a series of films with varying filler fractions. PFM h) Amplitude image and i) Phase image of PS-10. j) PFM displacement and phase-voltage curve. k) Piezoelectric voltages of a series of composite films with varying filler fractions. Finite element simulation of electrical field distribution in I) PVDF–HFP and m) SiO₂/PVDF–HFP model slab.

related to the bending vibration of Si–OH. The broad peak at 3450 $\rm cm^{-1}$ is attributed to –OH groups on SiO_2 surface. $^{[18]}$

Piezoresponse force microscopy (PFM) verify the piezoelectric property of the composite SiO₂/PVDF–HFP-10 film. The amplitude pattern (Figure 2h) exhibits clear piezoelectric signals that the amplitude patterns present mild homogeneous bandshape features with width of around 2 μ m. The phase image also presents phase deflection with features consistent with the amplitude pattern, verifying that the film piezoelectric properties correspond to film microstructures^[4] (Figure 2i). When applying a ramp voltage from -5 to 5 V, a phase loop was observed where the phase angle altered nearly 150 degrees during this voltage range, displaying a butterfly loop (Figure 2j). The piezoelectric coefficient (d_{33}) value is calculated to be 71.95 pmV⁻¹ from the gradient of the butterfly loop.^[3a] The power conversion performance is then measured in a close circuit. Compared with composite films with other filler fraction values, SiO₂/PVDF–HFP-10 generated the highest voltage pulse of 18 V in response to an applied pressure of about 50 N exerted by a mechanical motor (Figure 2k). Finite element simulations (FES) in Figure 2(I-m) further indicates that the SiO₂ particle fillers in the pores of the composite also present electrical potential in relation with PVDF matrix.

Proposed mechanism

It's surprising that the composite film fabricated using the catalytically inert components PVDF–HFP and SiO₂ can present remarkable H₂O₂ productivity under ultrasonic treatment at ambient conditions. The characterizations above demonstrate that the composite film SiO₂/PVDF–HFP-10 presents an opencircuit voltage of 18 V, and the productivity of H₂O₂ of 246 µmol L⁻¹ h⁻¹, which are both highest in the series of tested films with varying filler fractions. It's highly possible that the production of H₂O₂ is realized because the piezoelectric fields drive the chemical conversion of ambient H₂O and/or O₂ to H₂O₂. The standard potential of 2e⁻ oxygen reduction is 0.68 V vs. RHE,^[19] and H₂O/·OH transformation is 2.38 V vs. RHE.^[20] In order to deepen the understanding of the H₂O₂ production mechanism, a series of measurements and characterizations are further conducted.

Firstly, the contact angle (CA) of the series of $SiO_2/PVDF-HFP-X$ films are tested (Figure S4). With the increase of the SiO₂ filler fraction, the CA of ethanol aqueous solution (20 v

%) on the composite film increase. The CA of the ethanol solution is smaller than that of pure water, indicating that both SiO_2 component and ethanol enhance the contact among air, the aqueous state, and the composite film. The microscopic three-phase contact should be a prerequisite for the reaction to take place.^[21]

Subsequently, the influences of the atmosphere components are studied. N₂ (g) and O₂ (g) are then used to replace the ambient air in the experiments (Figure 3a). These experiments are conducted without ethanol as scavenger. After 1 hour of reaction, no hydrogen peroxide is detected when N₂ is saturated in both the gas phase and solution in a closed environment (N₂–CE), indicating that O₂ is necessary for the H₂O₂ generation, and no H₂O₂ is produced via water oxidation.^[22] When O₂ is introduced in both the atmosphere and solution phase (O₂–CE), the yield of hydrogen peroxide (25 µmol L⁻¹ h⁻¹) is 2.5 times that in the ambient air condition phase in an open environment (O₂–OE), the H₂O₂ productivity (18 µmol L⁻¹ h⁻¹) is 1.8 times that in the ambient air condition.



Figure 3. Mechanism study on piezoelectrical H_2O_2 generation from the SiO₂/PVDF–HFP-10 film (PS–X denotes SiO₂/PVDF–HF0P–X). a) Gas-replacement experiments that uses O_2 or N_2 to replace ambient atmospheres. CE denotes closed environment, OE open environment, and G gas phase. b) Scavenger experiments that employs no scavenger, EtOH, IPA, or NBT as the scavenger. EPR tests of c) SiO₂/PVDF–HFP-10 and d) PVDF–HFP. e) ATR-IR spectra, f) H_2O_2 generation, and g) the amounts of superoxide radicals generated by after replacing the hydroxyl groups in SiO₂/PVDF–HFP-10 with amino groups. h) H_2O_2 generation performance with varying particles sizes and i) ultrasonic power.

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These results demonstrate clearly that oxygen reduction reaction dominates the H_2O_2 production process, O_2 as reagent comes from both the dissolved oxygen in solution and the ambient oxygen. In addition, when only the gas phase in the sealed container is replaced with N_2 (N_2 –G), the generation of H_2O_2 could not be detected either, indicating that the majority of reagent oxygen originated from the atmosphere and the amount of dissolved oxygen or the oxygen trapped in-film cannot sustain the continuous production of H_2O_2 .

Thirdly, the role of the scavenger is explored by using isopropanol (IPA) and nitroblue tetrazolium chloride (NBT) instead of ethanol (Figure 3b). IPA is also able to consume ·OH resembling the scavenging effects of ethanol, and similar trend of improving the H_2O_2 yield from 10 µmol L⁻¹ h⁻¹ to 172 µmol L⁻¹ h⁻¹ is observed. In clear contrast, when adding NBT which consumes ${}^{\bullet}O_2{}^{-}$, the productivity of H_2O_2 is as low as 3 µmol L⁻¹. These probing experiments clearly indicate that superoxide radical is crucial for H_2O_2 generation. The removal of ·OH enhances reaction production.

EPR results provide direct evidence for the existence of $O_2^$ and $\cdot OH$ during the piezoelectric H_2O_2 production of SiO₂/ PVDF-HFP-10^[23] (Figure 3c). As expected, pure porous PVDF-HFP film without SiO₂ fillers present rather weak signals of ${}^{\bullet}O_2^{-}$ and no signals of ${}^{\circ}OH$, indicating that chemical conversion of ambient O₂ hardly takes place (Figure 3d). The SiO₂ filler contributes from two aspects to the overall chemical reaction process. The first aspect is that they enhance piezoelectrical response and generate higher surface potentials. The second aspect is that they provide surface hydroxyl groups for the adsorption of the active species. In order to highlight the important role of their surface hydroxyl groups, we blocked the SiO₂ surface with 3-aminopropyltriethoxysilane (Figure 3e) by coupling reaction.^[24] This step will only alter the surface groups from hydroxyls to amines without influencing the piezoelectrical response. We found that the surface-modified composite film cannot afford the H_2O_2 generation despite their high piezoelectrical response. Thus, the importance of the surface hydroxyl of SiO₂ in promoting the H₂O₂ generation is thus demonstrated. Further direct studies such as using in-situ characterization or using transient spectra technologies should be able to provide more detailed information. We are currently making efforts in such directions.

In-depth probing further corroboration that e⁻ available for chemical reactions reside around film surfaces. The direct evidence is that when ultrasonically treat the film in a solution of AuCl₄⁻, the AuNPs with diameters around 30–50 nm deposited on the SiO₂/PVDF–HFP film surface (Figure S5). When increasing the SiO₂ diameters from 15 nm to 500 nm which should decrease the number of three-phase boundaries, the H₂O₂ productivity also decreases from 246 µmolL⁻¹h⁻¹ to 109 µmolL⁻¹h⁻¹ (Figure 3h). It's understandable that the boundary area should present the highest piezoelectric voltage since SiO₂ particles chemically pole the PVDF–HFP matrix and enhance the β -phase formation therein. The SiO₂ provides oxygen-containing sites for hydrophilic species (ethanol, °O₂⁻, and °OH) to adsorb and the hydrophobic porous PVDF–HFP tends to accumulate O₂^[25] which different from hydrophilic

network of hydrogel.^[26] The synergistic existence of the piezoelectrically effective region (which attracts screening charges) and the gas-liquid-solid three-phase interface in the porous SiO₂/PVDF–HFP-10 film facilitates the chemical conversion reaction from O₂ to H₂O₂ to take place^[27] (Figure 1a).

The density of states (DOS) diagrams obtained from DFT calculations indicate that (Figure S6) the bandgap of the $SiO_2/$ PVDF–HFP composite is nearly unanimous with SiO_2 , being the typical value of classical oxide insulator. The results corroborate that the electron cross-band transition is difficult in the composite film and the screen charges from environment should be responsible for the oxygen reduction reactions.

The influence of the ultrasonic power on H_2O_2 production is then explored (Figure 3i). When the power enhances from 120 to 300 W, the catalytic performance is boosted remarkably. The enhanced ultrasonic power can strengthen the cavitation effect and lead to stronger mechanical oscillation, which in turn induces higher piezoelectrical potentials. The high piezoelectrical potential can induce higher screen charge densities around the film surface, lifting the redox power of the charges.^[28] Regarding the free charges, the piezopotential functions similar to bias in electrocatalysis which charges the electrons to climb over the thermodynamic barrier to launch electrochemical redox reaction.^[29]

Based on the above results, the mechanism for the effective H₂O₂ generation on SiO₂/PVDF–HFP-10 via ultrasonic motivation is proposed as follows and illustrated in Figure 4. The ORR reaction leading to H₂O₂ takes place around the boundary between SiO₂ and PVDF-HFP, where the piezoelectric field effectively functions around the solid-liquid-gas three-phase intersection. The SiO₂ functions i) as PVDF-HFP polarizing reagent to enhance the piezoelectric capabilities, where the enhanced polarization of samples is accomplished by hydrogen bond induction; ii) to trap the liquid component around the reaction area, and iii) to serve as the active adsorption site for the reaction to take place. Furthermore, synergies gained from ethanol and ample hydroxyl groups enhanced the wettability of samples, which enriched the active sites for water adsorption in the ORR process. The PVDF-HFP matrix provides the piezoelectric field under ultrasonic motivation as well as trap airphase around the reaction region. The surface screen electrons, which are screen charges from external environment accumulating against the internal depolarization field, enable the reduction reaction to take place.

During the reaction process, the rapidly changing and periodically mechanical oscillation caused by the ultrasonic irradiation induces the dynamic polarization of composite film. In this alternating electric field, the H–O bond of water molecules at the interface of SiO₂/PVDF–HFP undergoes non-negligible relaxation and further dissociate into H⁺ and OH^{-.[30]} They may form Si–OH with the dangling bonds on SiO₂ surface, such as Si–O– and Si–. More importantly, they may also serve as screen charges to participate reaction.^[31] The OH⁻ can be responsible for releasing secondary e⁻ and ·OH under periodic polarization change to facilitate the ORR.^[32] C₂H₅OH is oxidized to CH₃CHO by ·OH so as to accelerate the reaction forward to cross kinetic barriers.^[33] In the meantime, the hydrogen protons



Figure 4. Diagram of the proposed mechanism. i) Ionization of water molecules and the release of secondary electrons. ii) $2e^- O_2$ reduction around the gasliquid-solid interface. iii) Reaction starts when the piezopotential exceeds the 'threshold' potential or free charges inside SiO₂ are excited from valence band by the burst of cavitation bubble. iv) The chemical reaction processes in each step. *denotes the adsorption site.

and energized electrons will combine with the absorbed O_2 to form *OOH. Another possible source of the excited charges is from conduction bands of SiO₂. Cavitation bubble explosion widens the bandgap of SiO₂ to around 5.6 eV as suggested by DFT simulation, indicating that the CB electrons would present higher reducing power (Figure S8). At the same time, the electrons may gain enough energy to jump to higher energy band and present higher energy. These energized electrons should be able to push the chemical reaction of H₂O₂ generation according to the energy band theory. In the meantime, the surface adsorption of the active species on SiO₂ surface lower the transition energies between the intermediates. The effectively energized electrons and the decreased transition energy effectively accelerate the generation of H₂O₂ in the system.

To verify the ethanol oxidization, 4-Amino-3-hydrazino-5mercapto-1,2,4triazole (AHMT) was added to the mixture post reaction (Figure S7a). Following further addition of KIO_4 , the colorless solution turned purple (Figure S7b). Correspondingly, an absorption band arose at around 554 nm in UV-vis spectra (Figure S7c). This color change indicates the formation of aldehyde in the system. The Chemical reaction process in each step is exhibited in Eqs. (2–7).

$$H_2 O \rightarrow H^+ + OH^-$$
 (2)

$$OH^- \rightarrow \cdot OH + e^-$$
 (3)

$$^* + O_2 + e^- \rightarrow ^*O_2^- \tag{4}$$

$$^*O_2^- + H^+ \to ^*OOH \tag{5}$$

$$^{*}OOH + H^{+} + e^{-} \rightarrow ^{*} + H_2O_2 \tag{6}$$

$$C_2H_5OH + \cdot OH \rightarrow CH_3CHO + H_2O$$
⁽⁷⁾

Lastly, DFT calculations with a computational hydrogen electrode (CHE) model^[34] are then utilized for further compre-

hending the active site and the regulating mechanism of SiO₂ in the oxygen reduction process. The two-electron (2e⁻) pathway to H₂O₂ via oxygen reduction reaction (ORR) is considered based on above analysis. This pathway composed of two proton-coupled electron transfer steps with only one intermediate^[35] (*OOH). For an ideal 2e⁻ ORR catalyst to present high activity, the kinetic barrier for O₂ adsorption should be minimal, and the barrier for *OOH to be further reduced or decomposed (to *O)should be maximized to assure high selectivity.^[36] Meanwhile, the adsorption of intermediate should be thermally balanced at equilibrium potential as U=0.7 V versus RHE, where the free energy of *OOH is approximately equal to 3.52 eV.^[37] Shown in Figure 5a, the adsorption barrier on the PVDF–HFP polymer (the model with $rac{1}{2}$ mark), SiO₂ without −OH (marked □), SiO₂, and SiO₂/PVDF−HFP composite are calculated. Those adsorbing model are displayed in Figure 5 (b-d), respectively. The adsorption barrier on PVDF-HFP is the highest, being around 1.7 eV. The adsorption on SiO₂ without hydroxyl group is rather strong, with an energy of around -1.0 eV, where the *OOH should be tightly trapped on SiO₂ surface and experience further reduction. In comparison, the adsorption on SiO₂ and SiO₂/PVDF-HFP composite are similar, being 0.6 and 0.8 eV, respectively. The mild adsorption energy should benefit H₂O₂ production. Thus, the reaction active sites should be the surface hydroxyls of SiO₂, where the intermediate *OOH can be properly stabilized for H₂O₂ production.

Conclusion

In summary, we have reported on a novel piezoelectrical H₂O₂ generation film. The H₂O₂ production active flexible film is composed of bio-safe and catalytically inert PVDF-HFP matrix and SiO₂ nanoparticle fillers. The effective H₂O₂ generation capability (246 μ mol L⁻¹ h⁻¹) stem from the synergistic existence of the piezoelectrical field and the air-liquid-solid three-phase regions around the porous film. This H₂O₂ production film is distinct from the previously reported piezoelectrical H₂O₂ generation materials in that (i) it presents the flexible film state, being easily applied and collect after use; (ii) it is composed of bio-safe component which are stable upon relative long-term storage in ambient conditions and free of oxidizing pressures against bio tissues in the resting state or decomposed; (iii) the film is easily produced and the production can be readily upscaled using current industrial methods. For the uniqueness of the reported H₂O₂ generation materials, we expect our report to promote the development of locally H₂O₂ generating materials and also provide novel scientific insights towards piezoelectrically motivated chemical reactions.



Figure 5. DFT calculation of the intermediate adsorption energy on various possible adsorption sites. a) Free energy diagram of $2e^-$ ORR on the samples. The adsorption model of *OOH on b) the PVDF–HFP polymer skeleton (marked $rac{1}$), SiO₂ without –OH (marked \square), c) regular SiO₂, and d) SiO₂/PVDF–HFP composite.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords: H_2O_2 generation \cdot piezoelectrical chemical conversion \cdot PVDF—HFP \cdot silica \cdot ORR

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