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Accelerated confined mass transfer in piezoelectric semiconducting metal—organic frameworks for H₂O₂ piezo-photosynthesis

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The piezo-photocatalytic O_2 reduction reaction offers a promising pathway towards H_2O_2 synthesis. However, in addition to rapid recombination of photogenerated electrons and holes, this gas-consuming reaction is inherently limited by O₂ dissolution and mass transfer dynamics. Here, energy band structures and dipole moments of piezoelectric semiconducting UiO-66 metal-organic frameworks (MOFs) are engineered by modulating functional groups ($-NH_2$, $-CH_3$, -OH, $-NO_2$ and $-F_4$) and metal nodes (Hf and Zr). This fine-tuning of MOF building blocks leads to an enhanced piezoelectric coefficient, gas capacity and light absorption to facilitate subsequent piezo-photocatalysis. Furthermore, the tunable band structure enables the construction of a Z-scheme heterojunction with another piezoelectric semiconductor. The resulting heterostructure CdS/NH2-UiO-66(Hf) with increased structural asymmetry exhibits further boosted piezoelectricity, leading to rapid charge separation and transfer due to the enhanced piezoelectric-induced built-in electric field. In addition, the piezoelectric semiconducting MOF serves as a tri-functional nanoreactor synergistically improving gas solubility, confined mass transfer, and O2 molecule activation under periodic piezoelectric deformation. Consequently, a H2O2 yield rate of 2079.1 μ mol g⁻¹ h⁻¹ is achieved without sacrificial agents or O₂ bubbling via coupling of piezocatalytic and photocatalytic effects. This study opens a new avenue for tailoring microenvironments to design highly efficient piezo-photocatalytic systems.

Introduction

Photocatalytic hydrogen peroxide (H₂O₂) production through the two-electron oxygen reduction reaction (ORR) is a sustainable alternative to the energy-intensive anthraquinone process without hazardous by-products.¹⁻⁴ Typically, this photocatalytic process is driven using traditional semiconductors by absorbing photons with energy exceeding their bandgap to generate electron-hole pairs, which subsequently migrate to the surface to catalyze redox reactions. Recently, piezoelectric semiconductors have emerged as building blocks to construct piezoelectric-assisted photocatalytic systems taking advantage of both piezoelectric and photocatalytic effects. Specifically, under mechanical stress, piezoelectric photocatalysts with polarity develop a built-in electric field through spatially

separated positive and negative charges, which facilitates the separation of photo-generated electron-hole pairs.⁵⁻⁷ Consequently, piezoelectric semiconducting materials, such as ZnO,^{5,8} BaTiO₃,^{9,10} C_xN_y,^{11,12} and covalent organic frameworks¹³ have been investigated for H₂O₂ synthesis through optimization strategies including doping,¹⁴ metal nanoparticle/single-atom decoration,¹⁵ construction of heterojunctions,¹⁶ crystal facet engineering,¹⁷ etc.

Recently, cadmium sulphide (CdS), as a typical piezoelectric semiconductor with excellent visible-light absorption, suitable energy band levels, structural versatility, and good piezoelectric response, has also been reported to catalyze the ORR to form $\rm H_2O_2$. However, the aqueous-phase ORR as a gas-consuming reaction is fundamentally constrained by $\rm O_2$ dissolution dynamics, where inadequate reactant delivery to catalytically active sites leads to mass-transport bottlenecks. Accordingly, porous architectures, such as hollow carbon spheres and zeolite, have been engineered to construct macroporous/microporous water to enhance gas solubilities. Horse strategy thereby establishes gas-enriched microenvironments at the catalyst–water interfaces, which is favorable for the gasconsuming reaction. Horse stables are supported to the gasconsuming reaction.

Therefore, piezoelectric semiconducting metal organic frameworks (MOFs) with tailored micropores may enable

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improved piezo-photocatalytic ORR to generate H₂O₂.^{6,29,30} Furthermore, as piezoelectric pumps have been used in microfluidics, piezoelectric MOFs can potentially act as peristaltic nano-pumps to expedite the gas diffusion process within the confined microporous water upon external force-induced deformation. Hence piezoelectric semiconducting MOFs could serve as multifunctional nanoreactors synergistically integrating gas confinement, directional mass transport, and catalytic activation within their well-defined and tailorable structures. Notwithstanding this, the application of MOFs in piezo-photocatalytic gas-consuming reactions is scarcely reported.31 UiO-66 is a prototypical zirconium-based MOF, characterized by its high stability, large surface area and tunable pore size. These properties make it highly promising for applications in gas storage/separation, catalysis, sensing, drug delivery, and photochemistry. 32-34 Notably, Zeng and co-workers demonstrated that UiO-66 nanocrystals often adopt a lowsymmetry, non-centrosymmetric structure, which endows them with piezoelectric properties.35 Given that the piezoelectricity of MOFs is governed by their polarity, density functional theory (DFT) calculations, well-suited for quantifying the changes in dipole moment induced by varying metal nodes and linker substituents, have been reported to reveal the underlying polarity and piezoelectricity differences. 6,30 Therefore, systematic investigation on piezoelectric semiconducting UiO-66 MOFs with tunable piezoelectricity, optical properties and porosity plays a pivotal role in elucidating structure-property relationships in piezo-photocatalytic systems.

Herein, a range of UiO-66 MOFs with different functional groups and metal nodes, with dipole moment determined by DFT calculations, were comprehensively examined. The synergistic variations in piezoelectricity, bandgap and specific surface area (SSA) emerge as the critical determinant governing their piezo-photocatalytic ORR performance. Upon integration with another piezoelectric semiconductor cadmium sulfide (CdS), the resulting structural asymmetric heterostructure demonstrated further increased piezoelectricity, resulting in enhanced separation and transport of photogenerated charge carriers owing to the piezoelectric-induced built-in electric field. The piezoelectric semiconducting MOF not only improved gas capacities and diffusion kinetics upon periodic deformation, but also activated the confined O2 molecules towards O2 formation. As a result, the CdS/MOF heterostructure achieved a H₂O₂ yield rate of 2079.1 μmol g⁻¹ h⁻¹ from air and water under concurrent excitation of light and ultrasonication. This work sheds light on the potential of piezoelectric semiconducting porous materials to break the bottleneck of photocatalytic gas-consuming reactions by improving gas solubility and mass transfer.

2. Results and discussion

2.1. Effects of functional groups and metal nodes on UiO-66 piezo-MOFs

First, a series of M-UiO-66(Zr)/(Hf) ($M = blank, NH_2, CH_3, OH, NO_2$ and F_4) MOFs with different functional groups and metal nodes were synthesized. To further establish heterostructures,

they undergo heat treatment with CdS in the subsequent synthesis process (vide infra). Therefore, the MOFs upon calcination at the temperature for heterostructure construction were denoted as NH2-UiO-Hf, UiO-Hf, NH2-UiO-Zr, F4-UiO-Hf, CH3-UiO-Zr, OH-UiO-Zr, NO₂-UiO-Zr, UiO-Zr and F₄-UiO-Zr, respectively. Powder X-ray diffraction (XRD) analysis confirmed the similar crystalline structures of the nine UiO-66-based MOFs (Fig. S1 and 1a). By comparing the XRD patterns and Fourier transform infrared (FTIR) spectra of the nine MOFs before and after calcination, UiO-Hf, CH3-UiO-Zr, OH-UiO-Zr, NO2-UiO-Zr, UiO-Zr and F4-UiO-Zr reveal no obvious change before and after calcination with good thermal stability (Fig. S1 and S2). Nevertheless, NH2-UiO-Hf, NH2-UiO-Zr and F4-UiO-Hf show broadening of the crystalline peaks after calcination, indicating disruptive effects on their crystalline structures. Fig. S3 shows their morphologies including the nanoparticulate structure for NH2-UiO-Hf, UiO-Hf, NH2-UiO-Zr, CH3-UiO-Zr, OH-UiO-Zr, NO2-UiO-Zr, and UiO-Zr and nanoflakes for F₄-UiO-Hf and F₄-UiO-Zr. Nitrogen adsorption-desorption measurements show that NH₂-UiO-Hf, NH2-UiO-Zr and OH-UiO-Zr have similar Brunauer-Emmett-Teller (BET) surface areas of 397.6 m² g⁻¹, 322.9 m² g⁻¹ and 315.2 m² g⁻¹, respectively. UiO-Zr and UiO-Hf show the largest BET surface area of 949.2 m² g⁻¹ and 836.7 m² g⁻¹, respectively, whereas F4-UiO-Hf and F4-UiO-Zr show the smallest SSA of 261.6 m 2 g $^{-1}$ and 262.4 m 2 g $^{-1}$, respectively (Fig. 1b and S4a). Despite the variation of SSA amongst the nine piezoelectric MOFs, their pore size distributions are similar, with an average pore size of 1.6 nm for NH₂-UiO-Hf, NH₂-UiO-Zr, F₄-UiO-Hf, CH3-UiO-Zr, OH-UiO-Zr, NO2-UiO-Zr, UiO-Zr, and F4-UiO-Zr, and 1.8 nm for UiO-Hf (Fig. S5a and b). The light absorption was measured using UV-vis diffuse reflectance spectroscopy (UV-vis DRS), as shown in Fig. 1c and S4b. It can be deduced that their absorption edges are at 466.2 nm, 311.6 nm, 455.9 nm, 339.7 nm, 335.1 nm, 378.0 nm, 392.4 nm, 318.7 nm and 369.0 nm, with the corresponding bandgaps of 2.66 eV, 3.98 eV, 2.72 eV, 3.65 eV, 3.70 eV, 3.28 eV, 3.16 eV, 3.89 eV and 3.36 eV based on the Tauc plots (Fig. S5c and d). Subsequently, their piezoelectric properties were investigated using piezoresponse force microscopy (PFM) as shown in Fig. 1d and S6. The piezoelectric hysteresis curves exhibit a typical butterfly shape under a ± 10 V DC bias electric field with phase changes of 180° in all samples. The effective piezoelectric coefficients d_{33} of NH2-UiO-Hf, UiO-Hf, NH2-UiO-Zr, F4-UiO-Hf, CH3-UiO-Zr, OH-UiO-Zr, NO2-UiO-Zr, UiO-Zr and F4-UiO-Zr are determined to be 78.31, 50.31, 39.15, 36.55, 33.46, 34.03, 47.51, 49.45 and 27.64 pm V⁻¹. To further unravel the effect of different functional groups and metal nodes on the piezoelectricity of the UiO-66 MOFs (Fig. S7), the dipole moments of four model MOFs were calculated using DFT. The 2D ELF basin analyses of NH₂-UiO-66(Hf), UiO-66(Hf), NH₂-UiO-66(Zr) and F_4 -UiO-66(Hf) are shown in Fig. 1e. The dipole moments of NH₂-UiO-66(Hf), UiO-66(Hf), NH₂-UiO-66(Zr) and F₄-UiO-66(Hf) were calculated to be -0.012, -0.006, -0.010 and -0.005 eÅ, respectively (Fig. 1f). The dipole moment of NH2-UiO-66(Hf) is larger than that of UiO-66(Hf), suggesting that the introduction of the -NH2 functional group enhances the polarity. The -F4 group, in contrast, weakened the polarity of the MOF. Meanwhile,

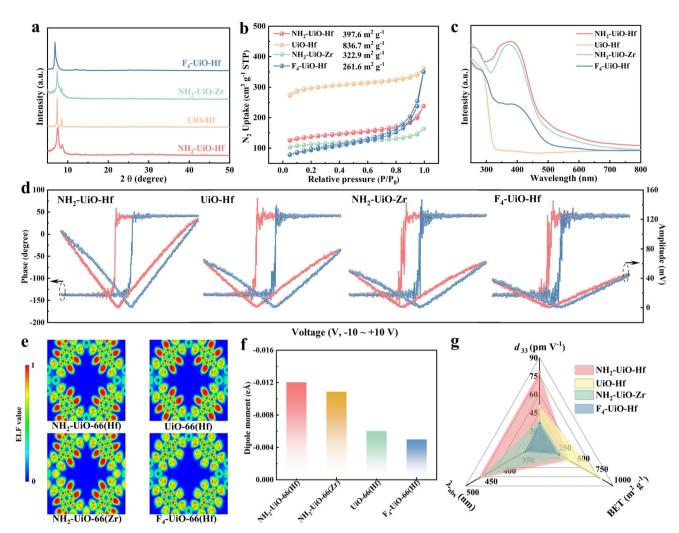


Fig. 1 (a) XRD patterns of NH₂-UiO-Hf, UiO-Hf, NH₂-UiO-Zr and F_4 -UiO-Hf upon calcination. (b) Nitrogen adsorption—desorption isotherms of NH₂-UiO-Hf, UiO-Hf, NH₂-UiO-Zr and F_4 -UiO-Hf. (c) UV-vis DRS of NH₂-UiO-Hf, UiO-Hf, NH₂-UiO-Zr and F_4 -UiO-Hf. (d) Piezoresponse amplitude—voltage and phase hysteresis loops of NH₂-UiO-Hf, UiO-Hf, NH₂-UiO-Hf. (e) 2D ELF basin analyses of NH₂-UiO-66(Hf), UiO-66(Hf), NH₂-UiO-66(Hf), UiO-66(Hf). (ELF value: 0 = fully delocalized, 1 = fully localized). (f) The corresponding calculated dipole moments. (g) Comparisons of the key parameters amongst NH₂-UiO-Hf, UiO-Hf, NH₂-UiO-Zr and F_4 -UiO-Hf.

NH₂-UiO-66(Hf) has a larger dipole moment than NH₂-UiO-66(Zr), which could be ascribed to the larger polarity of the Hf–O bond than that of the Zr–O bond. $^{36-38}$ It is noteworthy that the minor inconsistency of the trend between the calculated dipole moments and measured d_{33} could be due to the aforementioned disruptive effects upon calcination on their original structures. To conduct a comprehensive comparison, the key parameters of these MOFs with different functional groups and metal nodes are summarised in Fig. 1g, including SSA, d_{33} and light absorption edges. Notably, NH₂-UiO-Hf demonstrates well-balanced properties in all three metrics, which could be promising for piezo-photocatalysis as a microporous piezo-electric semiconductor.

2.2. Structural characterization of the CdS/NH₂-UiO-Hf heterostructure

A CdS/NH₂-UiO-Hf heterostructure was synthesized *via* a hydrothermal and post-assembly method (Fig. S8) and

subsequently characterized by XRD (Fig. 2a). The XRD pattern of CdS/NH2-UiO-Hf contains diffraction peaks of both CdS and NH2-UiO-Hf, which confirms the successful synthesis of heterostructures. This result is also observed in the XRD patterns of the heterostructure with various MOF contents, as the intensity of the two low-angle diffraction peaks of NH₂-UiO-Hf gradually increases with the increasing MOF weight percentage (Fig. S9). Moreover, Raman and FTIR spectra of CdS/ NH2-UiO-Hf also manifest that the individual CdS and MOF structure was maintained in the heterostructure (Fig. S10). In this designed heterostructure, piezo-MOF can serve as a gas reservoir by creating microporous water with high gas solubilities,26 with its piezoelectricity accelerating the gas diffusion process under mechanical vibration. Moreover, the CdS/NH2-UiO-Hf piezoelectric semiconductor heterojunction will facilitate the separation and transport of photogenerated electrons/ holes especially under the piezoelectric-induced built-in electric field, to participate in the subsequent redox reactions.

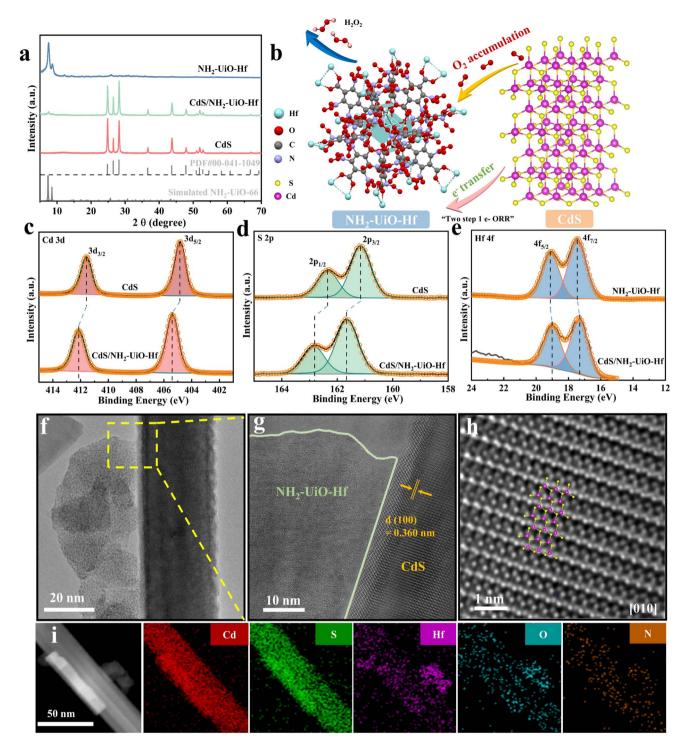


Fig. 2 (a) XRD patterns of NH_2 -UiO-Hf, CdS and CdS/ NH_2 -UiO-Hf. (b) Proposed piezo-photocatalytic reaction mechanism for the CdS/ NH_2 -UiO-Hf heterostructure. High-resolution XPS spectra of (c) Cd 3d, (d) S 2p, and (e) Hf 4f in CdS, NH_2 -UiO-Hf and CdS/ NH_2 -UiO-Hf. (f) HRTEM image of CdS/ NH_2 -UiO-Hf. (g) Enlarged HRTEM image of the yellow square. (h) HRTEM image of CdS in the heterostructure. (i) Corresponding elemental mapping of CdS/ NH_2 -UiO-Hf.

Fig. 2b illustrates the possible catalytic reaction pathways and mechanisms involved in the CdS/NH_2 -UiO-Hf heterostructure.

As shown in X-ray photoelectron spectroscopy (XPS) results (Fig. 2c–e), the characteristic peaks of Cd 3d and S 2p in CdS/ NH_2 -UiO-Hf were shifted to high binding energies in

comparison with CdS, whereas the binding energy of Hf 4f in the heterostructure, as compared to $\mathrm{NH_2\text{-}UiO\text{-}Hf}$, exhibits a negative shift of 0.2 eV. The shifting in their XPS spectra suggests electron transfer from CdS to $\mathrm{NH_2\text{-}UiO\text{-}Hf}$. The morphological features obtained by scanning electron

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microscopy (SEM) show that nanorod-like CdS displays an average length of 200-1000 nm (Fig. S11a), whereas NH₂-UiO-Hf consisted of octahedral-like particles with a feature size of around 40 nm (Fig. S11b). In CdS/NH2-UiO-Hf, the octahedrallike NH₂-UiO-Hf particles are uniformly decorated on the CdS nanorods upon post-assembly (Fig. S11c). The heterostructure and elemental distributions were further analysed using highresolution transmission electron microscopy (HRTEM). NH2-UiO-Hf, as shown in the dashed yellow square, is tightly attached to the smooth surface of CdS nanorods with intimate interface contact marked as a green line (Fig. 2f and g). In addition, CdS shows distinct lattice fringes with an interplanar spacing of 0.36 nm, corresponding to the (100) crystal plane of hexagonal wurtzite CdS (Fig. 2h).40 Energy-dispersive X-ray spectroscopy (EDS) elemental mapping confirms the coexistence of Cd, Hf, S, N and O, revealing distinct spatial segregation that aligns with the designed heterostructure (Fig. 2i).

Specifically, Cd and S are mainly distributed in the nanorod-like region, while Hf, N and O elements are predominantly localized within the rectangle-shaped particle region on the right side.

2.3. Piezo-photocatalytic performance evaluation

The performance of all catalysts was assessed for H₂O₂ production under light radiation and/or ultrasonic vibration in deionized water without O₂ bubbling and sacrificial agents (Fig. S12). First, the H₂O₂ production under catalyst-free conditions was negligible (Fig. S13). The piezo-, photo-, and piezo-photocatalytic performance of CdS/NH₂-UiO-Hf with various weight percentages of NH₂-UiO-Hf was examined, with the 15 wt% as the best-performing sample (Fig. S14). The H₂O₂ concentration using CdS, NH₂-UiO-Hf and CdS/NH₂-UiO-Hf catalysts exhibited quasi-linear accumulation over time, with good stability throughout the measurement period (Fig. 3a-c). As shown in Fig. 3d, the H₂O₂ yield rates of CdS/NH₂-UiO-Hf

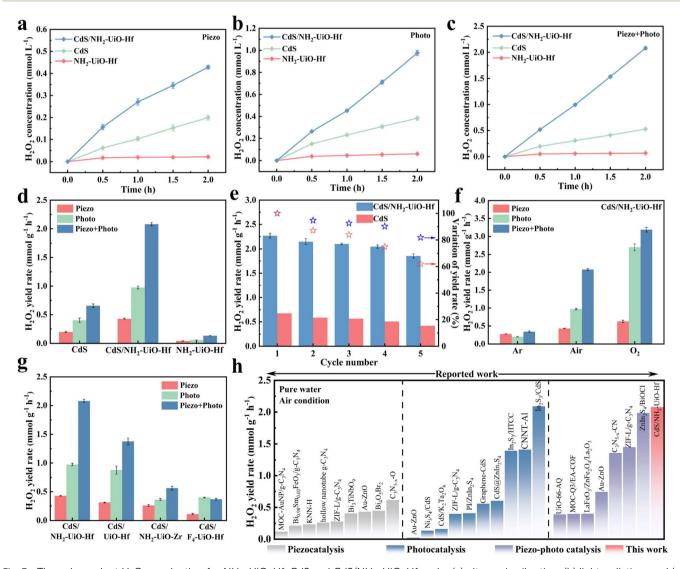


Fig. 3 Time-dependent H_2O_2 production for NH_2 -UiO-Hf, CdS and CdS/ NH_2 -UiO-Hf under (a) ultrasonic vibration, (b) light radiation, and (c) simultaneous ultrasonic vibration and light radiation. (d) H_2O_2 yield rates of NH_2 -UiO-Hf, CdS and CdS/ NH_2 -UiO-Hf. (e) Stability tests of CdS and CdS/ NH_2 -UiO-Hf. (f) H_2O_2 yield rates of CdS/ NH_2 -UiO-Hf under Ar, air and O_2 conditions. (g) H_2O_2 yield rates of heterostructures consisting of CdS and four model piezoelectric UiO-66-based MOFs. (h) Comparison of the H_2O_2 yield rates of CdS/ NH_2 -UiO-Hf with the reported catalysts.

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were much higher than that of pristine CdS and NH2-UiO-Hf under all three excitation conditions (i.e., piezo, photo, and piezo-photo). And their yield rates under piezo-photocatalytic conditions are significantly enhanced compared to that under either piezocatalytic or photocatalytic conditions. Furthermore, the performance of mechanically mixed samples is far inferior to that of the heterostructure (Fig. S15), which indicates that the construction of heterojunctions is favorable for the enhanced catalytic activity. It is worth noting that the optimum H₂O₂ yield rate of CdS/NH2-UiO-Hf under simultaneous ultrasonic vibration and light radiation reached up to 2079.1 μ mol g⁻¹ h⁻¹, which is 4.8 and 2.1 times higher than that under only ultrasonic vibration and light radiation, respectively. This suggests that the coupling of piezocatalytic and photocatalytic pathways significantly promotes H₂O₂ formation for CdS/NH₂-UiO-Hf. To reveal the stability of catalysts during the piezo-photocatalytic process, pristine CdS and CdS/NH2-UiO-Hf heterostructure were tested under the same conditions (Fig. 3e). CdS/NH₂-UiO-Hf maintained more than 80% of the original yield rate after five cycle tests, while the rate of CdS dropped to 60%, manifesting that the heterostructure can effectively slow down the corrosion with improved stability. Thereafter, XRD and SEM analyses were carried out for CdS/NH2-UiO-Hf after the stability test (Fig. S16) without noticeable changes compared to the as-prepared sample.

The H₂O₂ yield rates of CdS/NH₂-UiO-Hf under Ar, air and O₂ conditions were compared. As shown in Fig. 3f, the H₂O₂ production in an Ar-purged system was dramatically suppressed, while the H₂O₂ yield rate in an O₂-saturated system was increased compared to that under air conditions, which validates that the H₂O₂ yield predominantly originates from the ORR pathway. Subsequently, heterostructures consisting of CdS and various piezoelectric UiO-66-based MOFs were synthesised using the same methodology and tested for H2O2 production. The corresponding XRD patterns of these heterostructures are shown in Fig. S17. They showed pronounced variations in piezo-, photo- and piezo-photocatalytic H₂O₂ yield rates following the trend CdS/NH₂-UiO-Hf > CdS/UiO-Hf > CdS/NH₂-UiO-Zr > CdS/ F₄-UiO-Hf (Fig. 1g and S18). This could result from the difference in light absorption, piezoelectricity, photogenerated carrier behaviors and SSA of the MOFs, which in turn affect the overall piezo-photocatalytic H₂O₂ production of the heterostructures. Collectively, the CdS/NH2-UiO-Hf piezo-photocatalyst in water without scavengers and oxygen bubbling shows a performance advantage, compared to the state-of-the-art catalysts, as shown in Fig. 3h.8,18-22,41-56

2.4. Investigation of charge carrier behaviors

The charge separation and transfer behaviors of the catalysts were evaluated by transient photocurrent-time curves (TPC), electrochemical impedance spectroscopy (EIS) and steady-state photoluminescence (PL) spectroscopy. The TPC are shown in Fig. 4a, where the CdS/NH2-UiO-Hf heterostructure demonstrated the highest currents under all piezo-, photo- and piezophotocatalytic conditions. This implies efficient separation and transfer of carriers due to the formed heterojunction. In

addition, it can be found that the currents of all catalysts under piezo-photocatalytic conditions are larger than those under either photocatalytic or piezocatalytic conditions, suggesting an increased quantity of electron-hole pairs upon coupling of the piezocatalytic and photocatalytic effects. Similarly, arc radii of the heterostructure in EIS are all much smaller than those of bare NH2-UiO-Hf and CdS, indicative of its lowest charge transfer resistance (Fig. 4b). With respect to each sample, the arc radius under piezo-photocatalytic conditions is smaller than that under either piezocatalytic or photocatalytic conditions, revealing that the coupling effect of piezoelectricity and photocatalysis facilitates charge transfer. Furthermore, steady-state PL spectroscopy was conducted to unravel the radiative recombination dynamics of photogenerated carriers (Fig. 4c). The weaker PL intensity of CdS/NH₂-UiO-Hf than that of bare CdS implies a decreased radiative recombination of charges.

The optical properties and energy band structures of the catalysts were examined using UV-vis DRS, XPS and ultraviolet photoelectron spectroscopy (UPS) analysis. As shown in Fig. 4d, the catalysts have absorption edges in the range of 450-600 nm, presenting visible light absorption. In particular, the optical absorption edge of CdS/NH2-UiO-Hf showed a redshift to 580 nm compared with that of bare CdS and NH2-UiO-Hf. Meanwhile, the bandgaps of CdS and NH2-UiO-Hf were determined to be 2.38 and 2.66 eV through the Tauc plots (inset of Fig. 4d). As shown in Fig. S19a and b, the secondary electron cut-off edges (E_C) of NH₂-UiO-Hf and CdS are 19.31 eV and 17.52 eV, respectively. Hence, according to the equation work function (WF) = $21.22 \text{ eV} - E_C$, their WFs are calculated to be 1.91 eV and 3.70 eV. Valence band (VB) XPS spectra further show that the VB to Fermi level $(E_{\rm F})$ distances are 2.64 and 1.28 eV for NH₂-UiO-Hf and CdS, respectively (Fig. S19c and d). Using the equation $E_{\rm g}=E_{\rm VB}-E_{\rm CB}$, VB and conduction band (CB) positions of NH2-UiO-Hf are determined as 0.11 V and -2.55 V, respectively, and 0.54 V and −1.80 V for CdS.^{57,58} The energy band structures of CdS and NH2-UiO-Hf are illustrated in Fig. 4e. A schematic illustration of the charge transfer process of the CdS/NH2-UiO-Hf heterojunction during piezo-photocatalysis is shown in Fig. 4f. Upon contact between CdS and NH2-UiO-Hf, Fermi-level alignment leads to band bending and formation of a built-in electric field (IEF) at the heterojunction. Under illumination, the IEF drives the efficient separation of photogenerated electrons and holes, leading to the electrons migrating from CdS to NH2-UiO-Hf to form a Zscheme pathway for charge transfer. Under ultrasonic vibration, the piezoelectric polarization-intensified IEF further bends the energy bands, promoting carrier separation and transfer with suppressed recombination. 59-61

The mechanism of piezo-photocatalysis

The piezoelectric properties of CdS, NH₂-UiO-Hf and CdS/NH₂-UiO-Hf coated on a Pt substrate were investigated using PFM. As shown in Fig. 5a, all samples displayed characteristic 180° phase reversal and amplitude-voltage hysteresis loops under applied DC bias for piezoelectric materials, which are quite different from the signals of the non-piezoelectric Pt substrate (Fig. S20).62 The

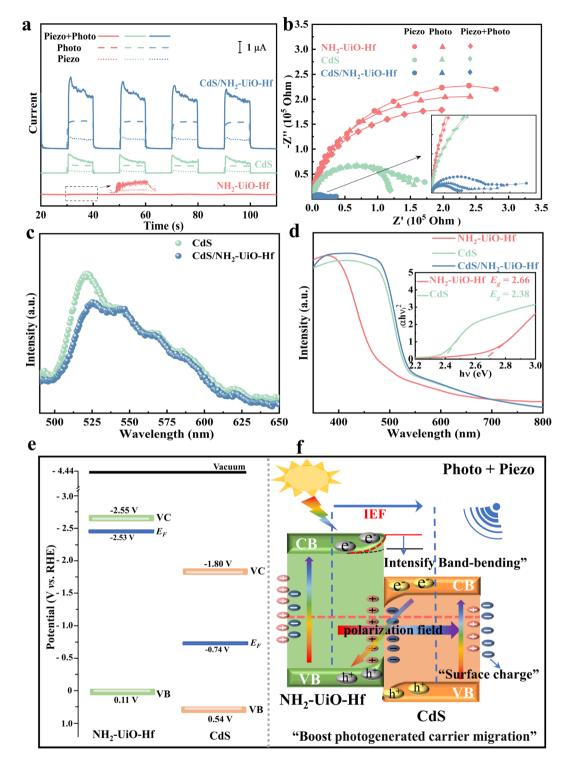


Fig. 4 (a) Transient photocurrent responses under piezo-, photo- and piezo-photocatalytic conditions. (b) EIS Nyquist plots, (c) steady-state PL spectra, (d) UV-vis DRS of the catalysts (inset: the corresponding Tauc plots). (e) Energy band structure of NH2-UiO-Hf and CdS. (f) Schematic illustration of the charge transfer process of the CdS/NH2-UiO-Hf heterojunction during piezo-photocatalysis.

 d_{33} values were determined to be 78.31, 93.54, and 141.31 pm V⁻¹ for NH2-UiO-Hf, CdS and CdS/NH2-UiO-Hf, respectively. The piezoelectricity of CdS/NH2-UiO-Hf was considerably enhanced compared to that of bare CdS and NH2-UiO-Hf, which could be ascribed to the increased structural asymmetry upon heterostructure assembly.63 The corresponding PFM topography height,

amplitude and phase images of CdS/NH2-UiO-Hf are shown in Fig. 5b, c and S21. Additionally, the piezoelectric properties of NH2-UiO-Hf, CdS and CdS/NH2-UiO-Hf were further evaluated by fabricating piezoelectric nanogenerators (PENGs) (Fig. 5d). The open-circuit voltages (V_{oc}) generated by NH₂-UiO-Hf, CdS and CdS/NH2-UiO-Hf under stimulation by an external force were 1.9

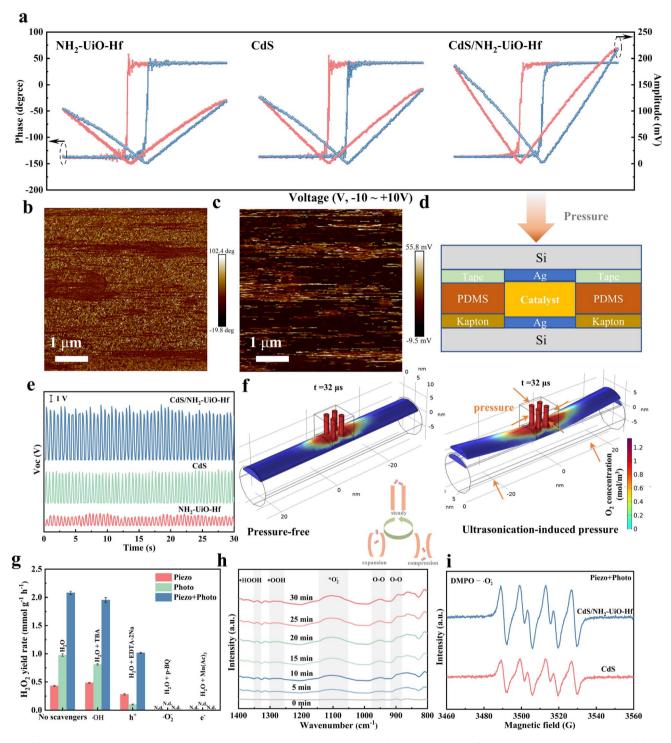


Fig. 5 (a) Piezoresponse amplitude–voltage and phase–voltage curves of NH₂-UiO-Hf, CdS and CdS/NH₂-UiO-Hf. PFM images of the (b) phase and (c) amplitude of CdS/NH₂-UiO-Hf. (d) Schematic diagram of the piezoelectric nanogenerator. (e) Open circuit voltages of the piezoelectric nanogenerator using NH₂-UiO-Hf, CdS and CdS/NH₂-UiO-Hf catalysts. (f) Finite element simulation results of O_2 transport in the heterostructure under ultrasonication-induced cyclic deformation. (g) Piezo-photocatalytic H₂O₂ yield rates of CdS/NH₂-UiO-Hf during the trapping experiment of the active species. (h) *In situ* FTIR spectra of CdS/NH₂-UiO-Hf in deionized water under illumination. (i) EPR spectra of DMPO- $^{\bullet}O_2^{-}$ generated over CdS and CdS/NH₂-UiO-Hf during piezo-photocatalysis.

V, 5.2 V and 8.6 V, respectively (Fig. 5e), indicative of their good piezoelectric properties.

To unravel the mechano-fluidic regulation mechanism of a piezoelectric porous MOF under ultrasonic stimulation, a cubic model with dimensions of $8 \times 8 \times 8 \text{ nm}^3$ was used to represent the piezoelectric NH₂-UiO-Hf nanoparticle, while cylinders with a radius of 6 nm and a length of 58 nm were employed to simulate the CdS nanorod (Fig. S22). Coupled finite

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element simulations (FESs) incorporating deformation, piezoelectricity, and mass transfer were performed on this heterostructure. The FES framework included dual boundary configurations: gas-phase simulations with top-inflow/openflank boundaries and liquid-phase simulations with designated inlet/outlet pairs, enabling systematic comparison of O₂ transport in static versus dynamically deformed channels. By imposing ultrasonic-mimetic periodic deformation (static → tensile → compressive cycling), an enhancement in O2 diffusion distance within the deformed channel was observed compared to the static control (Fig. 5f and S23), with accelerated concentration front propagation evidenced by gradient analysis. This enhancement stems from phase-synchronized pore volume modulation: tensile expansion generates negative pressure driving rapid external O2 influx, while subsequent compression converts elastic energy into kinetic momentum for directional gas ejection. The corresponding surface stress distributions and piezo-potential distributions upon ultrasonicinduced deformation are shown in Fig. S24b, d and S25. The simulations also reveal that light irradiation influences the O₂ transfer process via the photothermal effect (Fig. S26). The lightinduced heating drives non-isothermal diffusion, resulting in a noticeably higher O2 concentration at the front end of the orifice by t = 10 s under illumination, in direct contrast to the low concentration observed without light (Fig. S27). Cumulative cycling effects facilitate mass transfer for the O2 reduction reaction through stress-guided transport pathways, demonstrating that piezoelectric pore deformation triggers programmable microfluidic pumping for microenvironment engineering.

To investigate the piezo-photocatalytic reaction pathway towards H₂O₂ formation on CdS/NH₂-UiO-Hf, tert-butanol (TBA), EDTA-2Na, p-benzoquinone (p-BQ), and $Mn(Ac)_3$ were used as hydroxyl radical ('OH), hole (h+), superoxide radical ('O₂⁻) and electron (e⁻) scavengers for the trapping experiment of active species. As shown in Fig. 5g, EDTA-2Na, Mn(Ac)₃ and p-BQ significantly suppressed the H₂O₂ yield, proving that h⁺, e⁻ and 'O₂ play a crucial role during the H₂O₂ formation process. The minor effect of TBA on H2O2 yield conclusively eliminates 'OH as a primary reaction intermediate. To further identify the key intermediates over CdS/NH2-UiO-Hf during the formation of H₂O₂ under light illumination, the in situ FTIR spectrum was employed (Fig. 5h). The grey region exhibits progressively intensified peak signals with increasing reaction time. The O-O bond vibrational modes were observed at two distinct wavenumbers of 890 cm⁻¹ and 948 cm⁻¹. The peaks at 1106 cm^{-1} , 1290 cm^{-1} and 1342 cm^{-1} are attributed to $\mathrm{^*O_2}^-$, $\mathrm{^*OOH}$ and *H₂O₂ intermediates, respectively.^{22,65,66} In addition, prominent vibrational signatures of free H2O2 molecules were detected in the 2840-3062 cm⁻¹ wavenumber range, providing direct evidence for successful H2O2 generation (Fig. S28).64,66 To gain further insight into the key intermediate 'O2", electron paramagnetic resonance (EPR) was employed using 5,5dimethyl-1-pyrroline N-oxide (DMPO) as the radical trapping agent. Fig. 5i illustrates that both CdS and CdS/NH2-UiO-Hf exhibit the typical six-line characteristic peaks of DMPO-'O2⁻ under piezo-photocatalytic conditions, while the signal intensity of CdS/NH2-UiO-Hf is much higher than that of bare CdS, suggesting the enhanced 'O2" generation through the incorporation of MOFs. Therefore, it can be concluded that the piezo-photocatalysis follows a two-step one-electron ORR pathway $O_2 \rightarrow *O_2^- \rightarrow *OOH \rightarrow *HOOH \rightarrow H_2O_2$.

3. Conclusions

In summary, based on the comprehensive investigation on a series of piezoelectric semiconducting MOFs with distinct metal nodes and substituents of the linker, we establish systematic design principles for engineering MOF-based piezophotocatalysts with high activity. Further construction of heterojunctions consisting of the optimum MOF and another piezoelectric semiconductor results in a remarkably improved piezo-photocatalytic H_2O_2 yield rate of 2079.1 μ mol g^{-1} h^{-1} in the absence of a sacrificial agent and O2 bubbling. This performance enhancement originates from increased structural asymmetry with a stronger piezoelectric-induced built-in electric field, which drives the separation and migration of photogenerated electron-hole pairs participating in the subsequent redox reactions. Meanwhile, the piezoelectric effectinduced periodic deformation modulates the local microenvironment by improving gas capacities, diffusion kinetics, and O₂ activation within the micropores of MOFs. This work provides rational guidelines from initial MOF design to heterostructure post-assembly for developing highly active MOF-based piezophotocatalysts.

Author contributions

G. L. and Y. L. conceived the idea. Y. L., L. G., J. Q. and J. L. conducted the experiments and analyzed the synthesis, performance and characterization data. M. Y., J. Z. and G. L. guided and supervised the conduct of this research and provided financial support. Y. L. and G. L. wrote the manuscript and B. S., M. Y., W. T., J. Z., and G. L. edited the manuscript. All authors discussed the results and commented on the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

The data supporting the findings of this work are available within the article and its supplementary information (SI). Raw data supporting the findings of this work are available from the corresponding author upon reasonable request. Supplementary information: materials, synthesis procedures, characterization, DFT calculations, supplementary performance testing, and finite element simulation results. See DOI: https://doi.org/ 10.1039/d5sc07619f.

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