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Janus Covalent Organic Framework Films With Macroscopic Directional Carrier Migration for Switchable Gas Sensing

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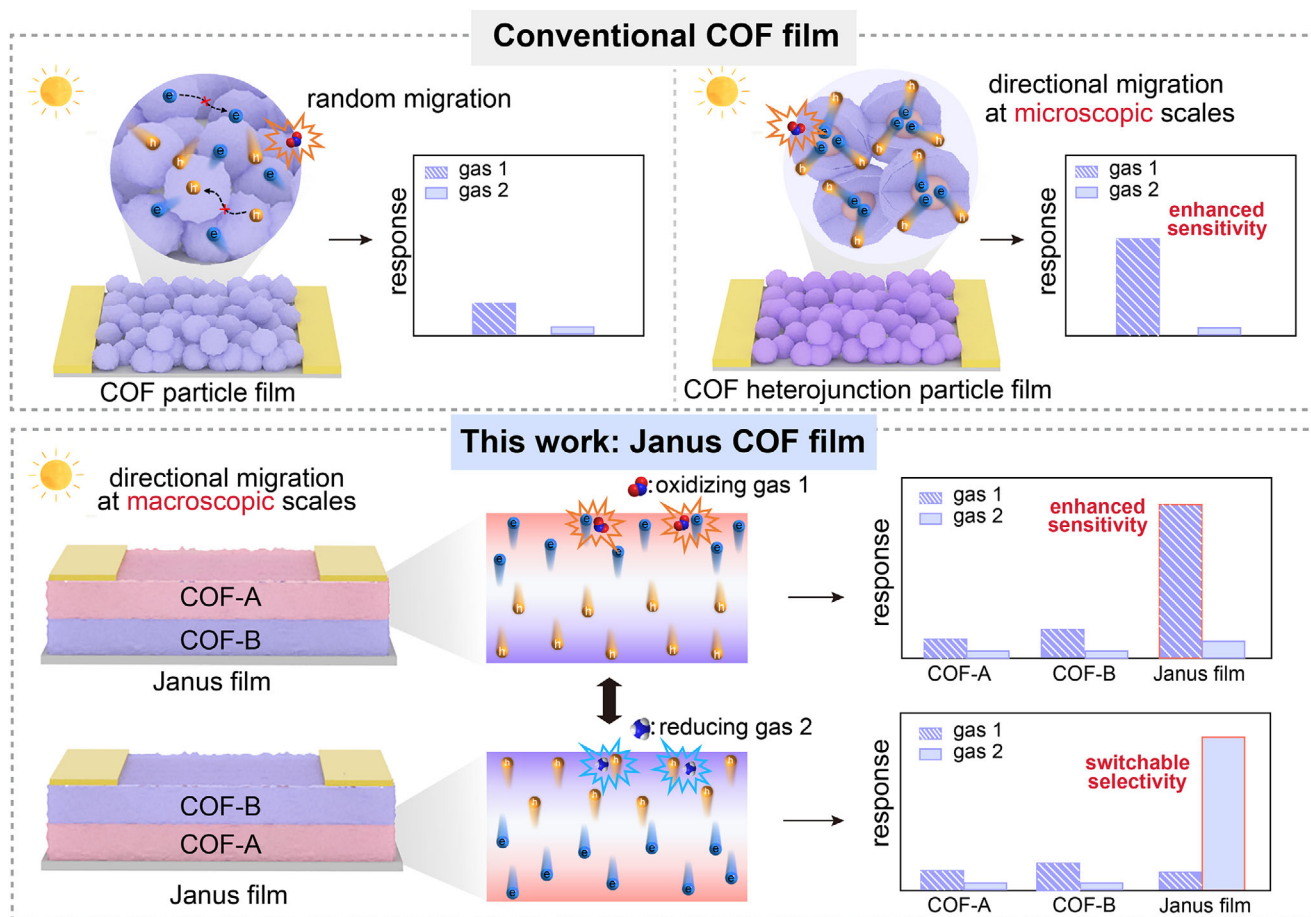
ABSTRACT

Macroscopic directional migration of photogenerated carriers in covalent organic framework (COF)-based heterojunction films is typically hindered by random carrier diffusion and interfacial structural disorder. In this study, we report for the first time the construction of sequence-controlled Janus COF films from lattice-matched isorecticular COFs (COF-366/COF-366-OH). The intimate interfacial assembly and the energy-level offset induce a built-in electric field that drives electrons and holes to migrate directionally toward opposite sides across the entire film. This asymmetric charge distribution endows the two sides of the film with distinct redox activities, enabling switchable and highly sensitive detection of both oxidizing and reducing gases by simply flipping the film. Such a unique feature is unprecedented for a single film. Moreover, the response of Janus COF film surpasses that of single-component counterparts by 5.2-fold for NO₂ and 5.3-fold for NH₃. This work offers a general strategy for macroscopic directional carrier migration in COF films and paves a new route for advanced sensing materials.

1 | Introduction

Covalent organic frameworks (COFs) have emerged as a promising class of optoelectronic candidates due to their long-range ordered crystalline structures, precisely tunable bandgaps, and flexible functional group modifications [1–5]. However, for previously reported COFs, the photogenerated carriers migrate primarily in a random diffusion manner [6, 7]. As a result, most electrons rapidly recombine with holes, severely limiting the efficiency of charge separation and utilization. This drawback significantly restricts the application of COFs in catalysis, photodetection, and smart sensing [8–10]. Aiming to overcome this bottleneck, various material design strategies have been

developed [11–15], including metal doping, bandgap engineering, and heterojunction construction [16–19]. Among these strategies, the construction of heterojunctions via coating COFs on semiconductor particles (e.g., metal oxides, metal-organic frameworks, or other COFs) is highly promising [20–24]. At the micro- and nano-scale, the interfacial built-in electric field enables efficient charge separation and directional migration inside a single heterojunction particle (Scheme 1) [25]. In contrast, once these particles are packed into thick films for the practical device fabrication, the resultant structural disorder and high interfacial resistance severely impede the transport of carriers across the macroscopic electrode (Scheme 1). Hence, realizing continuous charge transport pathways spanning from individual particles to



SCHEME 1 | Schematic comparison of conventional COF films and Janus COF films in photogenerated carrier migration regulation and gas sensing performance.

the entire film device to facilitate macroscopic directional carrier migration remains a critical challenge.

To overcome this bottleneck, we first construct sequence-controlled Janus COF films using two isorecticular COFs (COF-366 and COF-366-OH) with near-perfect lattice matching (Scheme 1). This intimate interfacial assembly avoids the structural mismatch commonly found in traditional heterojunctions. At the COF/COF interface, the slight energy-level offset induces the formation of built-in electric field that drives photogenerated electrons and holes to migrate toward opposite sides across the entire film, endowing the two sides with completely different redox activities. Consequently, the Janus COF film not only exhibits superior gas sensitivity but also demonstrates switchable sensing selectivity toward oxidizing and reducing gases. Such a unique feature has never been achieved in single films. Remarkably, the response of Janus COF film surpasses that of single-component counterparts by 5.2 times (to NO_2) and 5.3 times (to NH_3) by simply flipping the film.

2 | Results and Discussion

COF-366 was synthesized via a condensation reaction between 5,10,15,20-tetrakis(4-aminophenyl) porphyrin (TAPP) and terephthalaldehyde (TPA) (for details, see the Method Section in

Supporting Information) [26, 27]. In the crystal structure of COF-366, each TPA molecule was connected to two TAPP molecules, forming 2D π -conjugated macromolecular layers in the *ab* plane (Figure 1a). Subsequently, 2,5-dihydroxyterephthalaldehyde (2OH-TPA) was introduced into the synthesis system of COF-366 as replacements for TPA, resulting in the formation of COF-366-OH. Powder x-ray diffraction (PXRD) patterns showed that the phase structures of COF-366 and COF-366-OH are consistent with those of simulated COF-366 (Figure S1). A prominent adsorption band centered at 1622 cm^{-1} in Fourier-transform infrared (FT-IR) spectra was assigned to the stretching vibration of imine $\text{C}=\text{N}$ bonds (Figure S2).

Under the same solvothermal conditions employed for the synthesis of COF-366, pre-treated sapphire substrates were immersed in the reaction system with the front side oriented downward to prepare COF-366 thin films (for details, see the Method Section in Supporting Information). Through a secondary solvothermal growth process, two bilayer COF-366 thin films were fabricated on the sapphire substrate: one with COF-366-OH as the top layer and COF-366 at the bottom, named COF-366-OH-on-COF-366, while the other had the stacking order reversed, named COF-366-on-COF-366-OH (Table S1). The PXRD patterns revealed that both monolayer and bilayer COF-366 thin films exhibit high crystallinity, with their phase structures being consistent with that of the simulated COF-366 (Figure 1b). Two clear

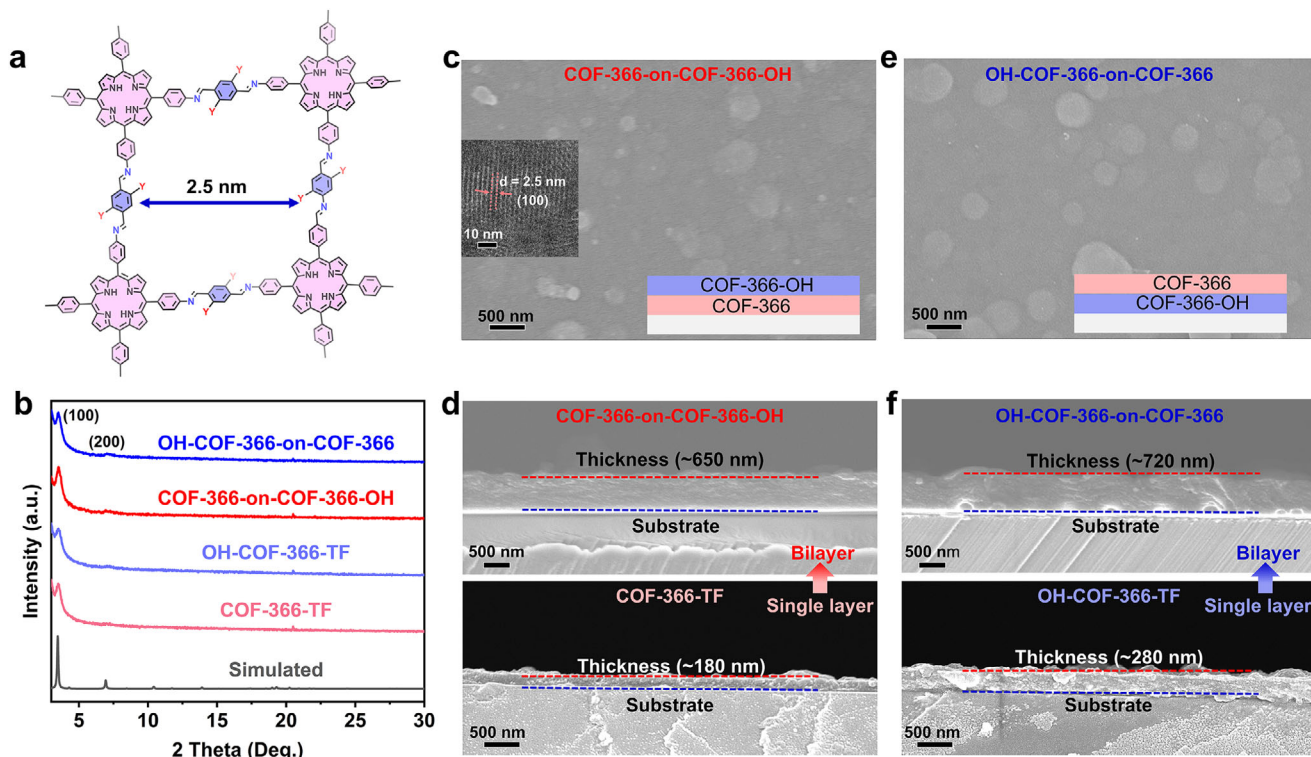


FIGURE 1 | (a) Structure of COF-366 and COF-366-OH. (b) PXRD patterns of COF-366 thin films. (c, d) Plan and cross-sectional view of COF-366-OH-on-COF-366 (inset: high-resolution TEM images). (e, f) Plan and cross-sectional view of COF-366-on-COF-366-OH.

diffraction peaks at 3.48° and 6.96° corresponding to the (100) and (200) diffraction peaks, respectively, were observed, indicating that these films were highly oriented (Figure 1b). These results suggested that COF-366 was successfully grown on the sapphire substrate using the bottom-up method [28].

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) tests were employed to investigate the morphology of these thin film materials. For single-layer thin films, COF-366 and COF-366-OH exhibited uniform and continuous thin film surfaces, as revealed by SEM images (Figure S3). After secondary growth, COF-366-OH-on-COF-366 and COF-366-on-COF-366-OH still maintained a uniform and continuous surface, with their thickness increasing from 180 nm (COF-366 thin film) to 650 nm and from 280 nm (COF-366-OH thin film) to 720 nm, respectively (Figures 1c–f and S4). These results suggested that COF-366 and COF-366-OH thin films have successfully undergone secondary growth. Furthermore, optical images showed that bilayer COF-366 thin films had deeper color than the single-layer (Figures S3 and S4). In the high-resolution TEM image of COF-366-OH-on-COF-366, the oriented lattice fringes could be observed and the lattice spacing of 2.5 nm was attributed to the (100) crystal face of COF-366 (Figure 1c) [26]. This further confirmed that the thin film deposited on the sapphire substrate is crystalline, and well-ordered COF-366. Additionally, two single-component bilayer COF-366 thin films were prepared for subsequent comparison. Optical images indicated that two single-component bilayer COF-366 thin films exhibited deeper colors than the single-layer COF-366 films, and PXRD patterns also revealed their high crystallinity (Figures S5 and S6).

The energy-level structures of COF-366 and COF-366-OH were determined through Ultraviolet–visible Adsorption Spectra (UV-vis) and Mott–Schottky (MS) measurements (Figures S7 and S8) [29, 30]. With the functional group transition from H to OH in COF-366, the valence band (VB) shifted from -5.68 to -5.64 eV, while the conduction band (CB) shifted from -3.97 to -3.90 eV (Figure S8). The energy-level relationships between COF-366 and COF-366-OH were staggered (Figure 2a). This specific arrangement of energy levels facilitated the formation of heterojunctions, thereby enhancing the separation efficiency of photogenerated electrons and holes [31–33]. To prove it, photocurrent tests were conducted (Figure 2b). Both COF-366-OH-on-COF-366 and COF-366-on-COF-366-OH exhibited higher photoconductivity compared to single-component bilayer COF-366 thin films (Figure 2b), indicating improved electrons–hole separation efficiency. These results suggested the successful construction of a heterojunction internally within COF-366-OH-on-COF-366 and COF-366-on-COF-366-OH.

Furthermore, the charge transfer directions in the bilayer COF-366 thin films under illumination were characterized using in situ x-ray photoelectron spectroscopy (XPS) [34]. The O 1s peak for COF-366-OH-on-COF-366 exhibited a shift of 0.10 eV toward higher binding energy upon light irradiation, indicating a reduction in electron density around oxygen atoms (Figure 2c). In contrast, the O 1s peak for COF-366-OH-on-COF-366-OH did not display a shift toward higher binding energy upon light irradiation, suggesting that the density of electron around oxygen atoms remained constant (Figure S9). This different variation in electron cloud density indicated that the electrons in COF-

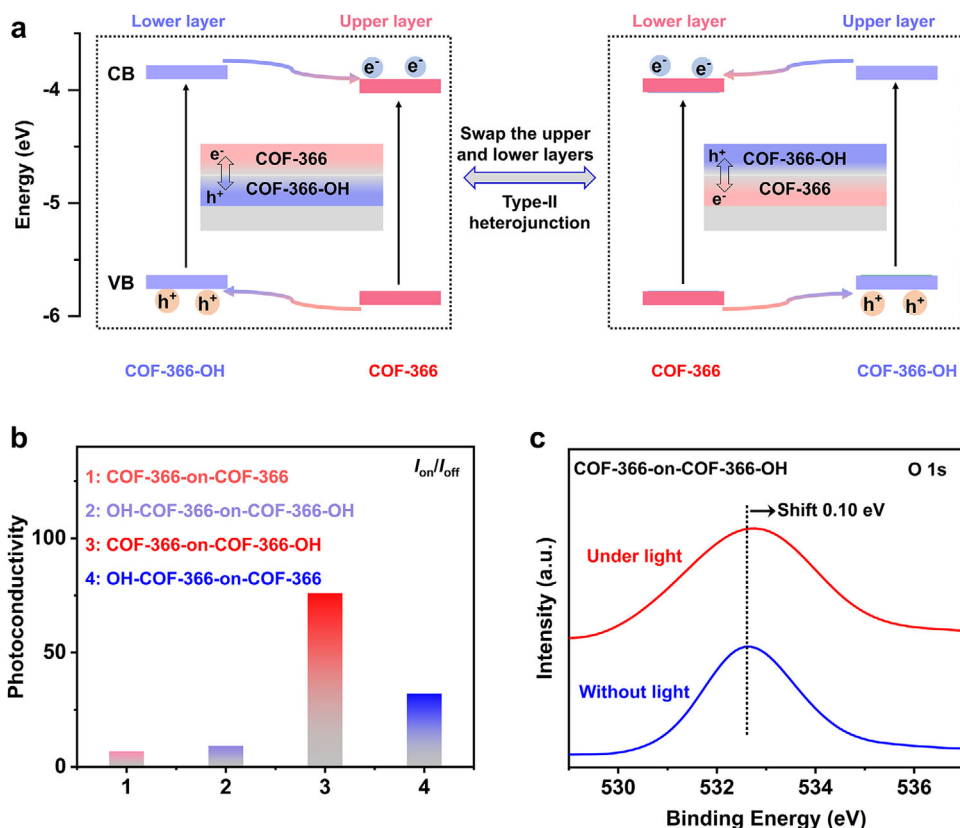


FIGURE 2 | (a) Charge-transfer process under light irradiation. (b) Photoconductivity measurements. (c) In situ XPS for O 1s under the dark and 420 nm light irradiation.

366-OH-on-COF-366 had a significant transfer from COF-366-OH to COF-366 under illumination. These in situ XPS tests results effectively elucidated the charge transfer directions in COF-366-OH-on-COF-366 and COF-366-on-COF-366-OH, confirming the successful establishment of a photoactive type-II heterojunction. The energy-level relationships and charge transfer directions of COF-366-OH-on-COF-366 and COF-366-on-COF-366-OH were illustrated in Figure 2a.

Bilayer COF-366 thin films with opposite stacking sequences form a type-II heterojunction that drives electron-hole separation under photoexcitation [35–39]. The charge distribution is determined by the vertical order of donor (COF-366-OH) and acceptor (COF-366) layers (Figure 2a). In the COF-366-on-COF-366-OH configuration, the top acceptor layer accumulated electrons, whereas reversing the stack to COF-366-OH-on-COF-366 enriched the top donor layer with holes. Notably, in situ XPS reveals a clear decrease in electron density at the surface located ~450 nm above the buried heterojunction, suggesting hole enrichment at the top surface (Figures 1c–f and 2c). This directly demonstrates that separated carriers at the heterojunction traverse the entire film and migrate to the surface. Leveraging this charge-separation behavior, we constructed Janus COF-366 films with an asymmetric charge distribution via a sequence-controlled integration strategy. The highly oriented, isorecticular structure provides a uniform interface and perfect lattice matching, generating a continuous built-in electric field and transport channels that enable macroscopic directional migration of photogenerated carriers across the device.

To demonstrate this macroscopic carrier regulation, we further evaluated the chemiresistive gas sensing performance of this series of bilayer COF-366 thin films using a home-made system [40]. For the fabrication of sensing test devices, silver wires were adhered onto the surface of each film with silver adhesive (Figure S10). Under visible-light and room-temperature conditions, these bilayer COF-366 thin films exhibited a positive response to 100 ppm NO₂ and a negative response to 100 ppm NH₃, consistent with the characteristics of p-type semiconductors (Figures 3a and S11–S13) [41–43]. Notably, two structurally inverted systems: COF-366-on-COF-366-OH and COF-366-OH-on-COF-366, demonstrated a reversed sensing selectivity from NO₂ to NH₃ (Figure 3a; Figures S11 and S12). In the former system, the top layer was electron-rich, exhibiting high selective response to NO₂. Conversely, in the latter, the top layer was hole-rich, conferring favorable selectivity toward NH₃. These results clearly indicated that, in this series of bilayer COF-366 thin films, the top layer functioned as the key sensing layer, playing a decisive and dominant role in determining the overall sensing performance. In contrast to conventional heterostructured gas sensing materials [44, 45], our Janus COF film enables switchable selectivity by simply flipping the film, which alternately presents an electron-rich surface toward oxidizing gases or a hole-rich surface toward reducing gases. Such functionality is intrinsically inaccessible in traditional heterojunctions and constitutes a genuinely novel feature for advanced gas-sensing applications.

For the COF-366-on-COF-366-OH, the top layer of COF-366 exhibited electron enrichment, resulting in a response to 100 ppm

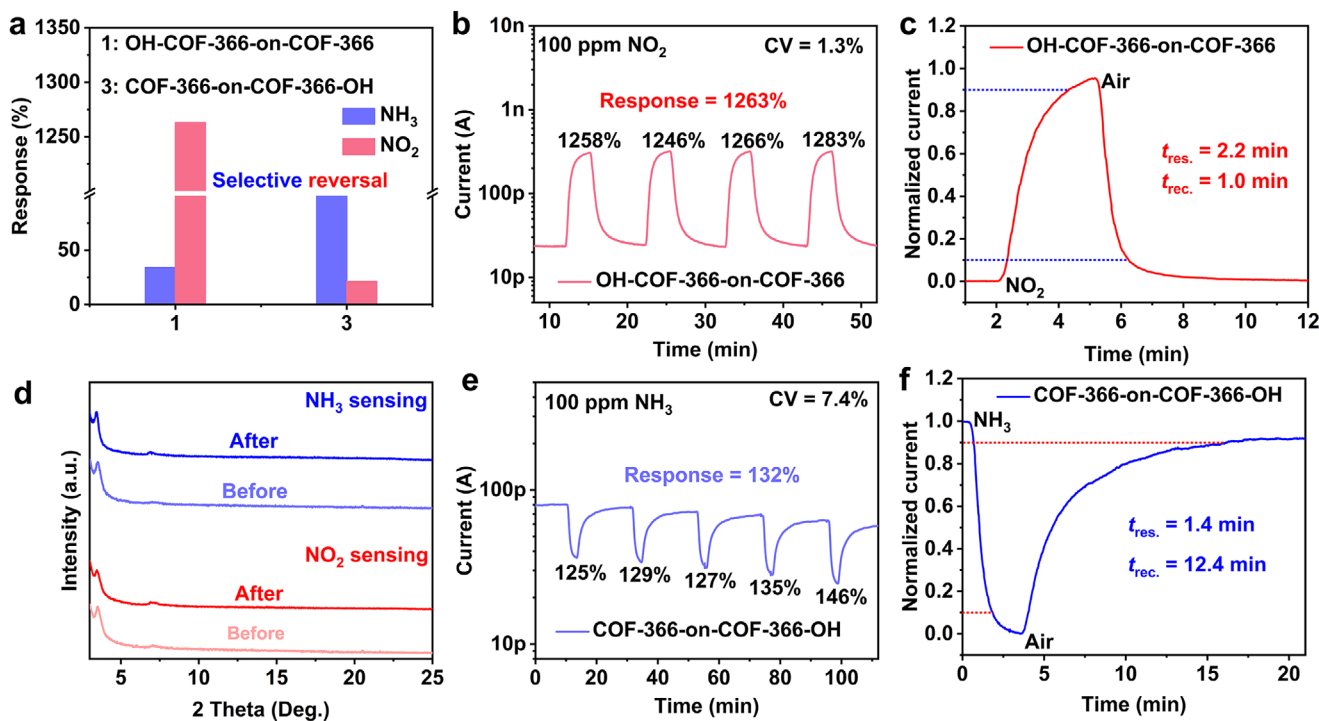


FIGURE 3 | (a) Response comparison toward NH₃ and NO₂. (b, c) Recycle response to 100 ppm NO₂ during 4 cycles and response/recovery time of COF-366-on-COF-366-OH. (d) PXRD patterns before and after sensing test. (e, f) Recycle response to 100 ppm NH₃ during 4 cycles and response/recovery time of COF-366-OH-on-COF-366.

NO₂ that reached 1263% (Figure 3b). This performance surpassed that of two single-component bilayer films (COF-366-on-COF-366 and COF-366-OH-on-COF-366-OH) effectively highlighting the improvement brought about by heterojunction construction (Figure S13). In four cycles, the coefficient of variation (CV) for the response to 100 ppm NO₂ was low (CV = 1.3%), indicating good cyclic stability and repeatability (Figure 3b). The response and recovery time were estimated to be 2.2 and 1.0 min, respectively (Figure 3c). The structure integrity of COF-366-on-COF-366-OH remained intact after 100 ppm NO₂ sensing test (Figure 3d). Additionally, COF-366-on-COF-366-OH exhibited a concentration-dependent response to NO₂ in the range of 1–100 ppm (Figure S11). The theoretical limit of detection (LOD) was calculated to be about 0.48 ppm from the simulated linear equation by setting the response to 10% (Figure S11).

In the case of COF-366-OH-on-COF-366, the top layer of COF-366-OH exhibited hole enrichment, leading to a response to 100 ppm NH₃ of 132% (Figure 3e). This outperformed the two single-component bilayer films (COF-366-on-COF-366 and COF-366-OH-on-COF-366-OH) (Figure S13). COF-366-OH-on-COF-366 also demonstrated excellent gas sensing performance in other parameters, like COF-366-on-COF-366-OH for NO₂ sensing, such as good cyclic stability (CV = 7.4%), fast response and recovery ($t_{res.}$ = 1.4 min and $t_{rec.}$ = 12.4 min), concentration-dependent response (Figures 3e,f and S12), and a low LOD of 5.6 ppm (Figure S12b). Similarly, the structure integrity of COF-366-OH-on-COF-366 remained intact after 100 ppm NH₃ sensing test (Figure 3d).

The sensing mechanism of bilayer COF-366 thin films was revealed through comparing XPS analysis before and after exposure to target gases (NO₂ or NH₃). After COF-366 was treated

with NO₂ mixed air, a new peak at 405.8 eV, corresponding to NO₂[−], appeared in the N 1s spectra, confirming the adsorption of COF-366 to NO₂ (Figure 4a) [46, 47]. Additionally, the N 1s spectra revealed that the ratio of C–N to C=N increased from 0.8 to 1.2, indicating the conversion of C=N to C–N after the NO₂ treatment (Figure 4a) [46]. These results demonstrated that the imine bond served as specific functional motif for NO₂ sensing. For the analysis of the NH₃ sensing mechanism, COF-366 was treated with NH₃-mixed air. The N 1s spectra revealed a peak at 398.1 eV (corresponding to C=N), which shifted to lower binding energy, indicating an increase in electron density around the C=N (Figure 4b) [48]. This result indicated that imine bond also serves as specific functional motif for NH₃ sensing.

The adsorption energies ($E_{ad.}$) of NO₂ on various functional units within COF-366 were calculated (Figures 4c and S14). The imine bond, hydrogen on aldehyde monomers, and porphyrin core all exhibited negative adsorption energies for NO₂, indicating attractive interactions (Figures 4c and S14). In contrast, the OH on aldehyde monomers displayed positive adsorption energies for NO₂, suggesting repulsive interactions (Figures 4c and S14). These results demonstrated that the imine bond was the favorable site for NO₂ adsorption among these functional units. Similar trends were observed in the adsorption energies of NH₃ on various functional units within COF-366 (Figures 4d and S15), with the imine bond again showing the highest affinity for NH₃ adsorption (Figures 4d and S15). Collectively, these findings indicated that the imine bond served as the key sensing functional motif within these thin films.

In this series of bilayer COF-366 thin films, the top layer played a crucial role in determining the sensing performance. For

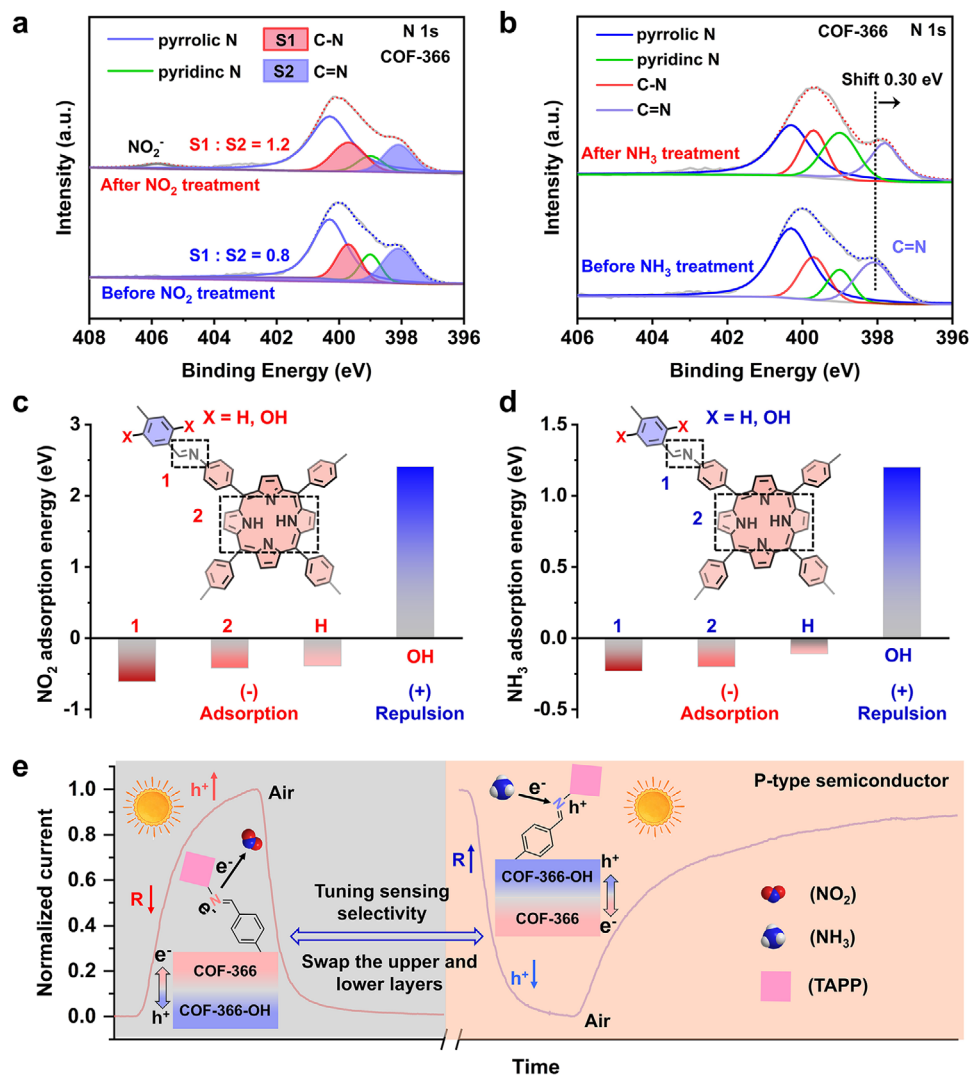


FIGURE 4 | (a, b) N 1s XPS spectra of COF-366 before and after 100 ppm NO₂ and NH₃ treatment. (c, d) Comparison of the NO₂ and NH₃ adsorption energy of the different sites on COF-366. (e) Possible gas sensing mechanism of COF-366-on-COF-366-OH and COF-366-OH-on-COF-366.

COF-366-on-COF-366-OH under illumination, the top COF-366 layer (an electron acceptor) accumulated many photogenerated electrons via the heterojunction. This facilitated efficient electron transfer with NO₂, leading to a change in conductivity (Figure 4e, left). In contrast, for COF-366-OH-on-COF-366, the top COF-366-OH layer (an electron donor) enriched photogenerated holes through the heterojunction, resulting in a strong response to NH₃ (Figure 4e, right). The ability to switch the sensing selectivity from NO₂ to NH₃ simply by inverting the top and bottom layers originated from the macroscopic regulation of carrier transport pathways within the film device. Specifically, the construction of Janus-structured COF-366 films established a continuous built-in electric field and directional charge carrier migration paths inside the device, enabling the oriented migration of photogenerated carriers throughout the entire film. Consequently, many carriers of the same polarity accumulated at the top layer, giving rise to a pronounced sensing response: when electrons accumulated at the top layer, the device exhibited a strong response to the oxidizing gas NO₂; when holes accumulated, it showed a marked response to the reducing gas NH₃. Thus, this reversal in sensing selectivity demonstrated that photogenerated charge

carriers underwent directional migration across the Janus COF-366 films. While such switchable sensing behavior is attractive, practical implementation of these Janus films within mixed-gas environments remains constrained by insufficient selectivity and inadequate interfacial durability. To tackle this bottleneck, the plasma-coupled electrochemical detection strategy developed by Jin et al. significantly improves selection flexibility and intrinsic sensitivity, providing a viable technological route for high-efficiency gas sensing [49, 50]. We envision that integrating this technique with our Janus film system offers the potential to overcome these existing limitations.

3 | Conclusion

In summary, we for the first time, tailored sequence-controlled Janus COF films from isorecticular COFs with near-perfect lattice matching. The intimate interfacial assembly and the energy-level offset induce the built-in electric field that drives macroscopic directional migration of carriers to opposite surfaces, realizing continuous charge transport pathways across the entire film

and endowing the two sides with distinct redox activities. In practice, simply flipping the film reverses the sensing selectivity toward oxidizing NO₂ and reducing NH₃. This unique feature is unmatched by any single film to date. Notably, the sensing performance of Janus COF films is more than 5-fold higher than that of single-component counterparts. This work offers a general design strategy for the macroscopic directional migration of carriers in COF films and paves a new route for advanced sensing materials and high-performance optoelectronic devices.

Author Contributions

Yong-Jun Chen: writing – original draft, conceptualization, formal analysis, data curation, validation, project administration. **Yi-Ming Xu:** software. **Zhi-Peng Luo:** formal analysis. **Guang-Ling Liang:** formal analysis. **Jiang-Feng Lu:** formal analysis, validation, funding acquisition. **Guan-E. Wang:** formal analysis, funding acquisition. **Shuang Wang:** writing – review and editing, writing – original draft, supervision. **Gang Xu:** writing – review and editing, funding acquisition, supervision, project administration.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

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

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting Information includes 15 Figures and 1 Table.

Supporting File: anie74942-sup-0001-SuppMat.pdf.