

# Unlocking persistent toluene degradation through self-defect modulation engineering via phosphorus-doping

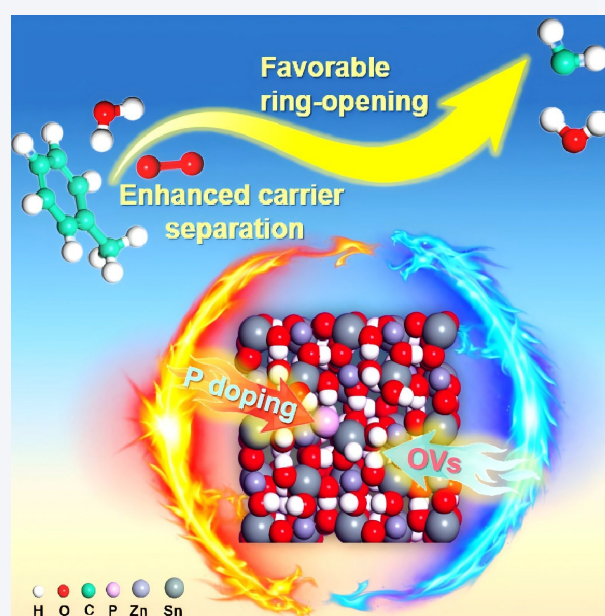
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**ABSTRACT:** The strategic design of photocatalysts with robust oxidative ability is essential for the efficient and sustainable elimination of volatile organic compounds (VOCs). Herein, we developed a phosphorus (P)-doped  $\text{ZnSn}(\text{OH})_6$  photocatalyst (ZHS-P50) with self-modulated defects via a one-step microwave hydrothermal method. The optimized ZHS-P50 exhibits impressive photocatalytic performance, achieving a toluene ( $\text{C}_7\text{H}_8$ ) removal efficiency of 95%. Notably, P incorporation modulates oxygen vacancy (OV) concentrations via self-defect regulation, creating a synergistic interplay that enhances molecular activation. This synergy promotes  $\text{O}_2$  adsorption and activation, leading to abundant generation of reactive oxygen species critical for photocatalysis. *In situ* spectroscopic analysis combined with theoretical calculations reveals that P doping and OVs facilitate the formation of benzoic acid as a key intermediate, accelerating ring-opening reactions and enabling deep mineralization. This work highlights ZHS-P50 as an efficient photocatalyst for  $\text{C}_7\text{H}_8$  abatement and establishes a defect-regulation paradigm for advanced oxidation catalysts.



**KEYWORDS:** photocatalysis, self-defect modulation,  $\text{ZnSn}(\text{OH})_6$ , mechanism, toluene

## 1 Introduction

Photocatalytic oxidation of toluene ( $\text{C}_7\text{H}_8$ ) is an environmentally friendly and efficient method for removing volatile organic compounds (VOCs) [1, 2]. The effectiveness of this process hinges on the design and synthesis of highly efficient photocatalysts. However, this field encounters several critical challenges: (1) Precise control of structure–performance relationship [3]. It is essential to precisely control the relationship between the structure and performance of photocatalytic materials. This involves optimizing the crystal structure, surface morphology, and electronic structure to improve catalytic efficiency [4]. (2) Accurate regulation of active sites [5]. The active sites on the surface of the photocatalyst need to

be precisely regulated, as their amount and distribution directly affect the oxidation capacity and selectivity of the catalyst [6]. (3) Control of intermediate products. Managing intermediate products is crucial. The reaction should not only convert VOCs into harmless end products but also prevent the generation and accumulation of secondary pollutants [7]. (4) Study of multiphase interface reaction kinetics. Research into the kinetics of multiphase interface reactions is vital for improving photocatalytic efficiency. It is necessary to explore the mechanisms of interface reaction and electron transfer, and understand their impact on the overall efficiency [8, 9].

As a typical perovskite-type hydroxyl compound,  $\text{ZnSn}(\text{OH})_6$  (ZHS) features a face-centered cubic structure and abundant hydroxyl groups [10]. The strong covalent bonds between Zn and Sn within ZHS significantly facilitate efficient charge carrier migration during photocatalytic reactions [11]. With these exceptional characteristics, ZHS emerges as a promising candidate for VOCs treatment [12]. However, pristine ZHS is limited by

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significant recombination of photo-carriers and insufficient active sites, which restrict its extensive application [13]. Oxygen vacancies (OVs), as intrinsic defects, can modify the local geometric structure of metal oxides, thus influencing the physical and chemical properties of metal oxide photocatalysts. Introducing OVs creates electron capture states that trigger additional charge transport modes, thereby improving charge separation efficiency. Importantly, an excessive concentration of OVs can occupy surface active sites, thereby impeding the photocatalytic reaction [14]. As a result, the precise regulation of OVs concentration is crucial for efficient photocatalytic reactions. Photocatalytic degradation of VOCs involves interactions with diverse gas molecules, necessitating an understanding of several key factors. The steric hindrance effect [15] originates from the repulsion between atoms or functional groups forced into close proximity due to geometric constraints within or between molecules. As documented [16, 17], for photocatalytic VOCs removal, photogenerated holes and electrons ( $e^-$ ) interact with  $O_2$  and  $H_2O$  on the surface of the photocatalyst, forming more superoxide radical ( $\cdot O_2^-$ ) and hydroxyl radicals ( $\cdot OH$ ), which then contribute to the degradation of the VOCs. Whereas  $O_2$  and  $H_2O$  can compete with target pollutants, such as  $C_7H_8$ , for active sites, resulting in steric interference. Hence, the steric-hindrance effect can impede the effectiveness of photocatalytic reactions. Despite this, few studies have focused on the impact of competitive adsorption due to steric hindrance on photocatalytic activity.

To address these challenges, it is essential to undertake suitable modifications to ZHS for boosting its photoactivity. Traditional defect-engineering approaches typically rely on creating a high density of OVs to boost carrier separation and adsorption activity. However, uncontrolled vacancy introduction often leads to structural instability and recombination centers, ultimately compromising photocatalytic durability. In contrast, self-defect modulation strategy couples heteroatom doping with vacancy repair, enabling the system to reach a thermodynamically favorable defect equilibrium and maintain optimal active-site density during synthesis [9, 18, 19]. Given the remarkable electron-donating capacity, adjustable valence state, and appropriate atomic radius, phosphorus (P) doping is an attractive approach for optimizing photocatalysts [8]. For example, Xue et al successfully induced the creation of positively charged centers ( $P^{3+}$ ) and negatively charged defect centers (indium vacancy ( $V_{In}$ )) in  $ZnIn_2S_4$  through P doping, leading to the efficient separation of electron-hole pairs [20]. According to the study by Ma et al. [21], P-modified  $BiSiO_5$  can improve the local charge distribution and facilitate the activation of small molecules. Dong et al. discovered that P doping into the structure of the multi-metal sulfide  $CoMo_2S_4$  optimized the electronic structure. As a result, the enhanced active surface effectively facilitated the adsorption and resolution of reactants and intermediates, enabling rapid charge transfer and favorable reaction kinetics [22]. Despite these advancements, the modification of ZHS with P doping has been scarcely explored.

In light of these considerations, we synthesized the cube-shaped ZHS photocatalyst incorporating P and OVs. The optimized sample (P-doped ZHS photocatalyst (ZHS-P50)) manifested exceptional degradation performance (95%) of  $C_7H_8$  under light irradiation. The synergistic interplay between defect self-modulation-mediated optimal OVs concentration and P doping establishes an efficient charge carrier transport and conversion pathway. Furthermore, by combining theoretical calculations and

experimental results, P doping and OVs can weaken the influence of steric hindrance, regulate the adsorption activation among small molecules, and promote the ring-opening degradation of key intermediates. This self-regulating defect evolution process introduces a new paradigm distinct from conventional vacancy-enrichment strategies and provides a dynamic route to stabilize catalytic active centers [23].

## 2 Experimental section

### 2.1 Samples synthesis

Tin tetrachloride pentahydrate ( $SnCl_4 \cdot 5H_2O$ , 99%), zinc acetate dihydrate ( $Zn(OAc)_2 \cdot 2H_2O$ , 99%), ammonium hydroxide solution (NaOH, 96%), and methylcellulose (99%) were purchased from Macklin. Sodium hypophosphite ( $NaH_2PO_2$ , 98%) was obtained from Picasso.

The photocatalysts were synthesized according to the following detailed processes: (1) 4 mL of  $SnCl_4 \cdot 5H_2O$  and 4 mL of  $Zn(OAc)_2 \cdot 2H_2O$  were mixed in Erlenmeyer flasks, stirred for 10 min on a magnetic stirrer ( $800\text{ r}\cdot\text{min}^{-1}$ ). (2) Afterward, different mass ratios of  $NaH_2PO_2$  (0%, 10%, 20%, 50%, and 80%) were dissolved in the abovementioned aqueous solution. (3) 4.6 mL of NaOH (3 M) and 20 mL of methylcellulose solution were added dropwise into above solution slowly to form a precipitate, followed by a stirring time of 30 min; then, the mixture was poured into a microwave-assisted hydrothermal synthesis instrument and maintained at  $120\text{ }^\circ\text{C}$  for 1 h. (4) After completion of the reaction, the reaction mixture was allowed to cool naturally to room temperature. After being washed three times with deionized water, the as-obtained white precipitate was dried at  $60\text{ }^\circ\text{C}$  for a period of 8 h. The obtained materials with different proportions according to the additive amount of  $NaH_2PO_2$  were designated as ZHS, ZHS-P10, ZHS-P20, ZHS-P50, and ZHS-P80, respectively. The illustration of sample synthesis process is shown in Scheme S1 in the Electronic Supplementary Material (ESM).

### 2.2 Sample characterization

The samples were examined by X-ray diffraction (XRD) equipped with  $Cu\text{ K}\alpha$  radiation (TD3500). X-ray photoelectron spectroscopy (XPS) spectra were obtained for the identification of the elemental compositions on material surface, using the C 1s peak as adventitious carbon. The energy dispersive spectrometer (EDS) was utilized to characterize the elemental distribution. Analysis of the surface morphology and microstructures of the as-obtained samples was inspected through scanning electron microscopy (SEM), transmission electron microscopy (TEM), and high-resolution TEM (HRTEM). The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) from 200 to 800 nm for the as-prepared photocatalysts were obtained by a UV-vis spectrophotometer (UV-2700, Japan). Recordings of light-induced reactive oxygen species (ROSs) were measured in a CIQTEK EPR200-Plus (Hefei) quartz capillary spectrometer during photoirradiation. The photoelectrochemical measurements were performed using an electrochemical station (CHI760E, China) with a standard three-electrode model, using  $Na_2SO_4$  solution (0.4 M) as the electrolyte. The prepared photoelectrodes were used as working electrodes, and the Pt foil and Ag/AgCl electrodes served as counter electrodes and reference electrodes, respectively. The electrochemical impedance spectroscopy (EIS) and Mott-Schottky (MS) curves were all

recorded using a CHI760E electrochemical workstation. The photoluminescence (PL) spectra and time-resolved PL (TRPL) were recorded on an RF-6000 FL spectrometer with an excitation laser wavelength of 320 nm. Using a Micrometrics specific surface analyzer (ASAP 2020) to acquire the surface area of the as-synthesized samples.

### 2.3 Photocatalytic activity evaluation

In a detailed procedure, 0.05 g of the as-obtained photocatalyst was uniformly dispersed across a quartz glass sheet. Next, four sheets with the photocatalyst loaded were placed within a reactor (200 mm × 100 mm × 17 mm), which was equipped with a quartz glass lid. A 300 W UV high-pressure mercury lamp with a wavelength of  $\lambda = 365$  nm was positioned vertically above the reactor to serve as the light source. Upon irradiation, gas monitors were employed concurrently to measure the concentrations of  $C_7H_8$ , dry air, and wet air. The total flow rate was set to 1 L·min<sup>-1</sup>. The initial degradation concentration of  $C_7H_8$  was set at 50 ppm. To control the temperature of the catalyst under 300 W UV irradiation during the photocatalytic oxidation of  $C_7H_8$ , a fan was installed outside the reaction chamber to provide continuous airflow. This measure effectively suppressed the thermal effects caused by prolonged UV exposure, maintaining the catalyst surface temperature within the range of 30–40 °C and minimizing interference from non-photocatalytic thermal factors during the reaction. A photoacoustic multi-gas analyzer (DKG-ONE, Duke Technology Co. Ltd.), as a multiple gas analyzer for continuous gas measurement, automatically sampled at 2 min intervals, recording real-time concentrations of  $C_7H_8$  and  $CO_2$ . Schematic diagram of the instrument was given in Scheme S2 in the ESM.

The  $C_7H_8$  conversion ratio ( $\eta$ ) was calculated as Eq. (1)

$$\eta = 1 - \frac{C}{C_0} \times 100\% \quad (1)$$

where  $C$  represented the  $C_7H_8$  concentration in the outlet steam, whilst  $C_0$  corresponded to the concentration in the inlet stream.

The  $C_7H_8$  mineralization ratio ( $M(\%)$ ) was calculated as Eq. (2)

$$M(\%) = \frac{C_2 - C_3}{C_0 \times 7} \times 100\% \quad (2)$$

where  $C_2$  stood for the real-time concentration of  $CO_2$  after the light was turned on, while  $C_3$  denoted the concentration of  $CO_2$  gas when the reaction chamber reached adsorption equilibrium in the dark.

### 2.4 Density functional theory (DFT) calculations

All calculations presented in this work were performed using the density functional theory within the Vienna *ab initio* simulation package [24, 25]. A ZHS slab model was constructed based on the experimentally confirmed cubic phase (PDF#20-1455). Considering the dominant exposed facet observed in HRTEM images, the (200) crystallographic plane was selected for surface modeling. A 3 × 3 × 1 supercell (192 atoms) was employed to represent pristine ZHS. For the P-doped model (ZHS-P50), P atoms were introduced into oxygen vacancy sites to simulate the experimentally observed defect modulation, with adjacent residual OV's retained after P incorporation. The pristine ZHS defect model (ZHS-2OVs) was constructed by introducing two surface OV's for comparison. A vacuum layer of 15 Å along the Z-direction was applied to eliminate periodic mirror interactions.

Electronic structure optimization was performed using the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [26]. The plane-wave cutoff energy was set to 400 eV, and the Brillouin zone was sampled using a 2 × 2 × 1 Monkhorst–Pack grid. The energy and force convergence criteria were 1 × 10<sup>-4</sup> eV and 0.02 eV·Å<sup>-1</sup>, respectively. The maximum atomic displacement step was 0.2 Å, with up to 60 self-consistent field (SCF) iterations per optimization cycle. After full relaxation, density of states (DOS), electron localization function (ELF), Bader charge distribution, and adsorption energies ( $E_{\text{ads}}$ ) were calculated to elucidate the electronic structure modulation and adsorption behavior associated with P doping and OV's. The atomic structure models of pristine ZHS and P-doped ZHS were optimized and are displayed in Fig. S1 in the ESM.

### 2.5 In situ diffuse reflectance infrared (IR) Fourier transform (FT) spectroscopy (DRIFTS) investigation

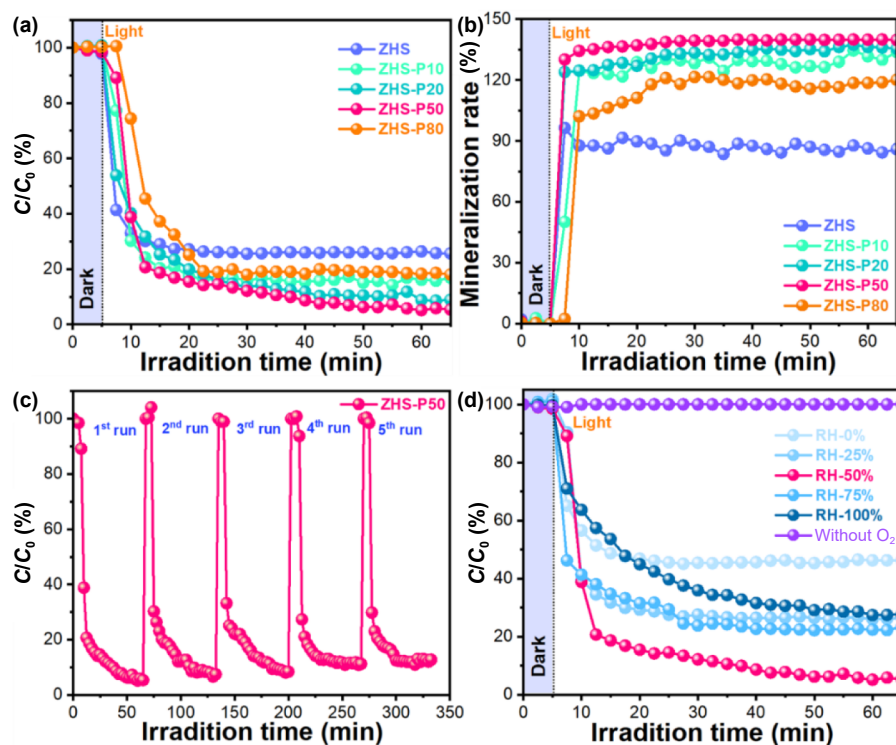
During the photooxidation of  $C_7H_8$ , the crucial intermediates of adsorption and reaction were investigated. The instrumental setup involved a TENSOR II FT-IR spectrometer (Bruker Corp.) with an *in situ* diffuse reflectance cell (Harrick, USA) as shown in Scheme S3 in the ESM. Prior to the test, KBr served as the base for the FT-IR spectra background. Firstly, the sample was heated at 150 °C and kept for 30 min to remove the adsorbed impurities on the surface; after that, the gas mixture (including  $C_7H_8$ ,  $O_2$ , and  $H_2O$ ) was charged into the reaction chamber and the real-time FT-IR spectra were tested every 2 min. Finally, the detection was carried out in the dark for 30 min to simulate the adsorption process of pollutants by photocatalysts. Subsequently, UV (MUA-165) irradiation conditions were applied for an additional 30 min.

## 3 Results and discussions

### 3.1 Photocatalytic removal of $C_7H_8$

As illustrated in Fig. 1(a), under UV light irradiation, the  $C_7H_8$  concentration decreases and then remains constant. Interestingly, the incorporation of P species significantly enhances the photoactivity of ZHS. It is worth noting that pristine ZHS only gives a 74% photooxidation of  $C_7H_8$ , while more than 95% removal rate is achieved over ZHS-P50. Moreover, ZHS-P50 exhibits a higher mineralization rate for  $C_7H_8$ , indicating less accumulation of toxic intermediate [27–30] (Fig. 1(b)). The multiple cycles of time-course curves were presented in Fig. 1(c), demonstrating the decent stability of ZHS-P50 within the experimental region [31]. Remarkably, during extended 720 min operation (Fig. S2 in the ESM), ZHS-P50 maintained stable activity with 95% removal rate. Additionally, XRD patterns and XPS spectra of ZHS-P50 before and after cycling (Fig. S3 in the ESM) show unchanged diffraction characteristics and nearly identical surface electronic states, confirming its robust crystalline and surface stability during photocatalysis. It is worth noting that the photocatalytic activity of ZHS-P50 is significantly superior as compared with other reported photocatalysts, as clearly shown in Fig. S4 in the ESM. Detailed data are exhibited in Table S1 in the ESM. Indeed, the initial concentration of  $C_7H_8$  in the reported photocatalysts ranged from 20 to 50 ppm.

As reported [32], the test conditions have a significant impact on the photoactivity. To clarify the relationship between humidity and photocatalytic activity, the photoactivity experiments under varying



**Figure 1** (a) The photocatalytic activity and (b) mineralization rate of the as-prepared samples. (c) Recycling measurements over ZHS-P50. (d) Photocatalytic  $C_7H_8$  efficiency under relative humidity (RH) of 0%–100% and without  $O_2$  over ZHS-P50. To evaluate the activation ability of as-obtained samples, pristine ZHS and those doped with phosphorus species were subjected to  $C_7H_8$  photocatalytic oxidation.

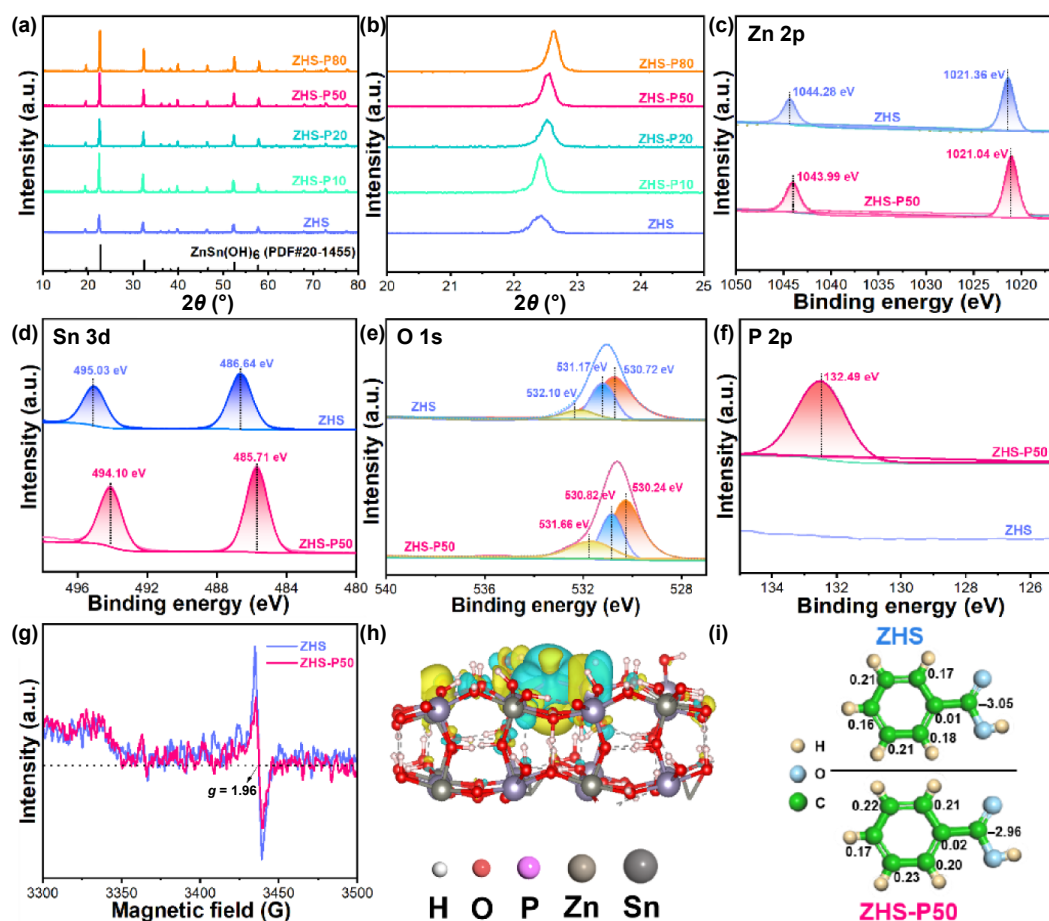
humidity conditions over ZHS-P50 were conducted. As presented in Fig. 1(d), an optimal removal efficiency can be achieved at a humidity level of 50%. This volcano-type behavior can be attributed to the balance between  $H_2O$ -assisted  $\cdot OH$  generation and competitive adsorption effects, where moderate water facilitates ROS formation while excessive humidity induces site blocking and steric hindrance for  $O_2$  activation. DFT calculations further reveal that P doping attenuates the surface chemical adsorption affinity toward  $H_2O$  (Fig. S5 in the ESM). Notably, under completely dry conditions (relative humidity at 0%), the loss of photoactivity was observed, highlighting the essential role of  $H_2O$  molecules in the reaction system to some degree [33]. Meanwhile, ZHS-P50 also exhibits decreased  $C_7H_8$  removal efficiency at 100% relative humidity, along with complete catalytic deactivation in the absence of  $O_2$ . These observations highlight the critical involvement of  $O_2$  in the mineralization of  $C_7H_8$ .

### 3.2 Confirmation of phase and structure

The crystal structures are explored by XRD measurements. As shown in Fig. 2(a), no distinguishable characteristic peaks could be observed, indicating that P doping has no obvious effect on the original crystal structure of ZHS. All the diffraction peaks correspond well to the tetragonal phase of ZHS (PDF#20-1455) [34]. Compared to pristine ZHS, the diffraction peaks shift to higher  $2\theta$  values after P doping, which is attributed to crystal lattice distortion [35] (Fig. 2(b)). The microstructures of powdery photocatalysts were examined using SEM measurements (Figs. S6(a) and S6(b) in the ESM). ZHS exhibits a typical cubic structure, and ZHS-P50 presents an analogous surface morphology, meaning that the original microstructure of ZHS remains unchanged. The HRTEM images reveal that both ZHS and ZHS-P50 have well-defined lattice fringes with a planar distance of 0.393 nm,

corresponding to the (200) plane of ZHS [11] (Figs. S6(c) and S6(d) in the ESM). EDS mapping confirms the presence of P species, showing even distribution of Zn, Sn, O, and P across the compounds (Figs. S6(e) and S6(f) in the ESM). To clarify whether the introduction of P species increased the specific surface area of ZHS-P50, subsequently, the Brunauer–Emmett–Teller (BET) specific surface areas ( $S_{BET}$ ) and pore size of ZHS and ZHS-P50 were determined using nitrogen adsorption/desorption isotherms and pore size distribution curves. As revealed in Fig. S7 in the ESM, the  $S_{BET}$  of ZHS and ZHS-P50 are 73.46 and 74.71  $m^2 \cdot g^{-1}$ , respectively, meaning that the specific surface area has a negligible effect on photocatalytic performance [36].

XPS measurements were subsequently conducted to investigate the electronic information on Sn, Zn, O, and P over the as-obtained photocatalysts. The peak positions of all peaks have been calibrated using the C 1s peak located at 284.8 eV. In the high-resolution XPS spectra of Zn 2p (Fig. 2(c)), the two peaks at binding energies of 1044.28 and 1021.36 eV correspond to the spin-orbit states of Zn  $2p_{1/2}$  and Zn  $2p_{3/2}$  in  $ZnSn(OH)_6$ , respectively [37]. The Sn 3d spectra of bare ZHS exhibit two contributions of Sn  $3d_{3/2}$  and Sn  $3d_{5/2}$ , which are located at 486.35 and 494.73 eV, respectively, indicating that the Sn element is ascribed to  $Sn^{4+}$  species (Fig. 2(d)) [11]. Moreover, in the case of Sn 3d and Zn 2p XPS spectra, the peaks of ZHS-P50 exhibit a  $\sim 0.3$  eV negative shift as compared with pristine ZHS, signifying the filling of OV by P doping, resulting in the formation of Zn–P–Sn bonds [20]. As depicted in Fig. 2(e), the O 1s XPS spectrum of bare ZHS can be divided into three peaks at 530.72, 531.17, and 532.10 eV, representing lattice oxygen (Sn–O and Zn–O), chemisorbed oxygen, and surface-adsorbed  $H_2O$  and hydroxyl groups [38, 39], respectively. As observed (Fig. S8 in the ESM), with P incorporation, the proportion of chemisorbed oxygen in ZHS-P50 decreases from 30.74% (ZHS)



**Figure 2** ((a) and (b)) XRD patterns of different samples. High-resolution XPS spectra of ZHS and ZHS-P50: (c) Zn 2p, (d) Sn 3d, (e) O 1s, and (f) P 2p orbitals. (g) EPR spectra for ZHS and ZHS-P50. (h) Charge density of P doping and Ovs-modified ZHS. (i) Calculated Bader effective charge of key intermediate.

to 27.44%, indicating a 3.3% reduction in OV-related species. This is due to the fact that there are more OVs in ZHS, resulting in an increase in the content of adsorbed oxygen [40]. In addition, it should be noted that ZHS-P50 also contains a peak centered at 132.49 eV, which is attributed to the P 2p signal, confirming the existence of P<sup>5+</sup> in ZHS-P50 (Fig. 2(f)) [39]. Moreover, the P content progressively increases with controlled variation of NaH<sub>2</sub>PO<sub>2</sub> concentration during synthesis (Fig. S9 in the ESM).

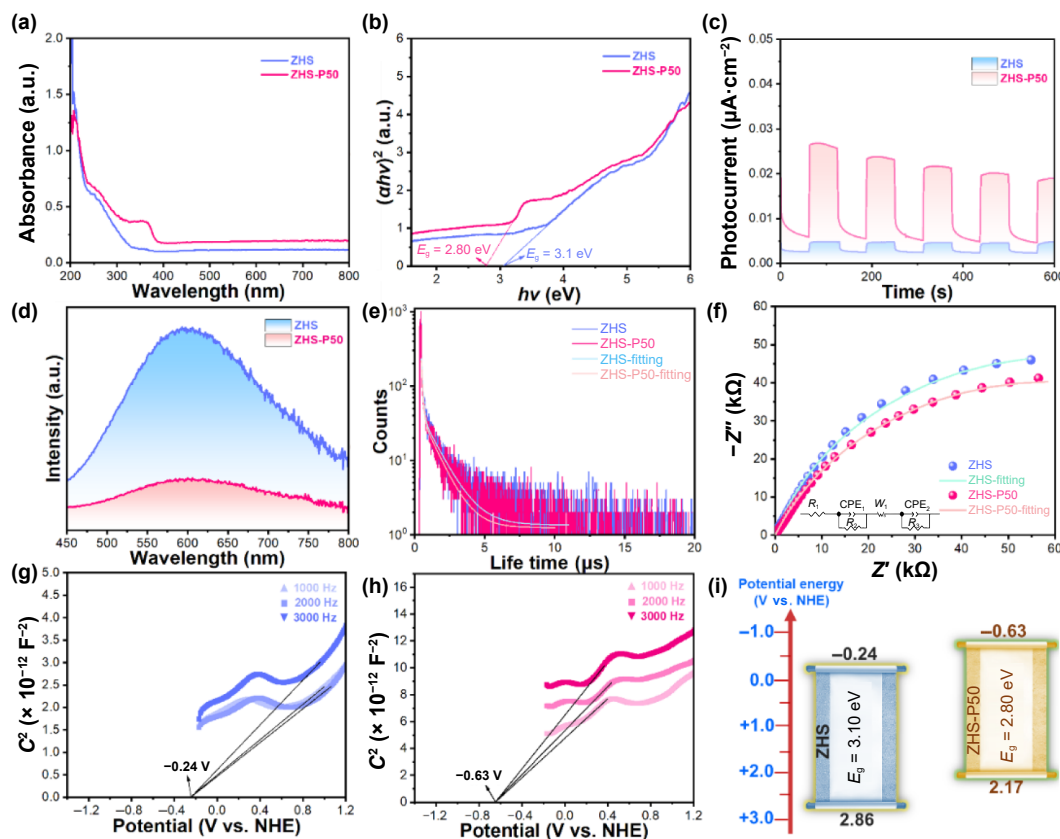
Furthermore, complementary Raman spectroscopic measurements were performed to further verify the defect evolution. In comparison with pristine ZHS, both the E<sub>g</sub> and A<sub>1g</sub> Raman bands of ZHS-P50 exhibit narrowed peak profiles, enhanced intensity, and negligible peak shifts, among which the Sn–O-associated A<sub>1g</sub> band shows the most remarkable changes (Fig. S10 in the ESM). As OVs generally disrupt the local symmetry of metal-oxygen octahedra and enhance phonon scattering, which typically leads to Raman peak broadening and intensity attenuation, this observation corroborates that P doping reduces lattice disorder, optimizes the local Sn–O coordination environment, and alleviates the lattice distortion induced by intrinsic OVs [41].

Consequently, these results indicate that P incorporation induces a self-defect modulation process, rather than completely eliminating OVs. This interpretation is further supported by the electron paramagnetic resonance (EPR) results shown in Fig. 2(g), where a strong EPR signal at  $g = 1.96$  is observed, originating from the unpaired electron trapped by Sn<sup>3+</sup> and OVs [42]. Such a signal

suggests that P doping drives the system toward a dynamic defect equilibrium state, in which partial vacancy filling and residual OVs coexist. Therefore, P doping regulates, rather than fully removes, OVs, leading to an optimized defect density for photocatalytic reactions [43]. As a result, ZHS-P50 can effectively reduce carrier recombination and push the progress of photocatalytic reactions. As shown in Fig. 2(h), the charge redistribution on the surface of the ZHS crystal was calculated based on the charge density difference simulations to further reveal the electron transfer mechanism. Specifically, the yellow and cyan regions indicate electron accumulation and depletion, respectively, confirming enhanced charge delocalization after P doping and OV modulation. This facilitates interfacial electron transfer and strengthens O<sub>2</sub> activation for subsequent C<sub>7</sub>H<sub>8</sub> ring-opening. P doping and the OVs of ZHS may improve the electronic conductivity, modify the electronic properties, and create more active sites for the ring-opening process of C<sub>7</sub>H<sub>8</sub>. This electron accumulation enhances the activation of benzene ring (Fig. 2(i)), making it more susceptible to subsequent ring-opening reactions.

### 3.3 Photo(electro)chemical properties

Photocatalytic reactions include three key steps: light absorption, photo-carrier migration, and surface reaction. As shown in Fig. 3(a), the absorption band of ZHS-P50 is slightly red-shifted compared to that of ZHS. The enhanced light harvesting ability can be observed in ZHS-P50, correspondingly owing to the



**Figure 3** (a) UV-vis DRS spectra of ZHS and ZHS-P50. (b) Tauc plots, (c) Photocurrent-time curves, (d) PL spectra, (e) TRPL spectra, and (f) EIS Nyquist plots of ZHS and ZHS-P50. Mott-Schottky curves of (g) ZHS and (h) ZHS-P50. (i) Band gap diagram.

introduction of P substitutes into the structure of ZHS [44]. Moreover, on the basis of Tauc plots, the bandgap values ( $E_g$ ) of ZHS and ZHS-P50 are estimated to be 3.1 and 2.8 eV in the inset of Fig. 3(b), respectively.

Indeed, the generation of ROSs is constrained by the availability of charge carriers resulting from photoexcitation, and thus it is necessary to carefully examine the dynamics of photogenerated charge carriers [45]. For this reason, EIS, PL, and photocurrent analysis were carried out to explore the charge transfer and separation behaviors. Figure 3(c) exhibits the apparent transient photocurrent response results of bare ZHS and ZHS-P50. Clearly, ZHS-P50 demonstrates significantly improved photocurrent generation as compared with ZHS, indicating superior photogenerated electron generation efficiency [46]. In addition, under 320 nm laser stimulation in PL spectra (Fig. 3(d)), ZHS-P50 exhibits a significant decay in the intensity of this band-to-band emission peak, signifying a lower electron-hole pair recombination rate [47]. TRPL fitting gives average lifetimes of 813.86 ns (ZHS) and 719.50 ns (ZHS-P50) (Fig. 3(e) and Table S2 in the ESM). We decoupled radiative  $K_R$  ( $K_R$  denotes the radiative recombination rate constant) and charge-extraction nonradiative  $\Delta K_{NR}$  ( $\Delta K_{NR}$  denotes the change in the nonradiative recombination rate constant associated with charge extraction), and the slightly higher  $K_R$  of ZHS-P50 excludes OV as recombination traps. Its shorter lifetime stems from a fast charge-extraction channel ( $\Delta K_{NR} = 0.16 \times 10^6 \text{ s}^{-1}$ ) driven by P-OV synergy to accelerate surface redox reactions [48].

To develop deeper into the charge carrier dynamics of the as-obtained photocatalysts. As seen in Fig. 3(f), a decreased arc radius in ZHS-P50 provides compelling evidence of a reduced charge

transfer resistance compared to that of bare ZHS [49]. As a result, in addition to significantly slowing down the recombination rate of photo-induced carriers, the P-doped layer acts as an electron mediator in ZHS-P50. Meanwhile, the conduction band (CB) of ZHS and ZHS-P50 are derived from Mott-Schottky plots [50], which are separately deduced to be  $-0.24$  and  $-0.63$  V (Figs. 3(g) and 3(h)). According to the equation  $E_g = E_{VB} - E_{CB}$ , where  $E_{VB}$  denotes the valence band (VB) edge potential, and  $E_{CB}$  denotes the CB edge potential [18], the relative energy levels of ZHS and ZHS-P50 are provided in Fig. 3(i), along with the  $E_g$  inferred from UV-vis DRS spectra.

### 3.4 Surface reaction

Adsorption, being the first step in photocatalytic surface reactions, is also the most critical one. To elucidate the contribution of P doping and OVs on the adsorption of molecular  $\text{H}_2\text{O}$  and  $\text{O}_2$  as well as  $\text{C}_7\text{H}_8$ , theoretical simulations were carried out to evaluate the adsorption behavior. To elucidate the individual and synergistic contributions of P doping and OVs while accurately reflecting the experimentally observed defect configurations, three representative models were established, including pristine ZHS containing abundant OVs (ZHS-2OVs), P-doped ZHS without OVs (ZHS-P), and P-doped ZHS with moderate residual OVs (ZHS-P-OVs). Specifically, ZHS-2OVs represents the abundant intrinsic OVs in pure ZHS, ZHS-P isolates the sole contribution of P dopants in the absence of OVs, and ZHS-P-OVs models the optimized state of ZHS-P50 after self-defect modulation, wherein P partially fills the OVs to achieve the experimentally verified coexistence structure. The charge density distributions under the effect of  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_7\text{H}_8$ ,

and the coexistence of the three were systematically calculated, as presented in Fig. 4(a) and Fig. S11 in the ESM. By comparison, ZHS-P-OVs shows obvious covalent interactions with molecular  $O_2$ , as evidenced by the significant electron density overlap between P/OVs sites and  $O_2$  molecules. This result confirms the synergistic role of P doping and OV in  $O_2$  activation, with an adsorption energy of  $-2.32$  eV, while the concomitant electron cloud enrichment on ZHS-P-OVs surface indicates enhanced interfacial electron transfer [34]. This occurs because the P atom directly injects electrons into the  $O_2$  antibonding orbitals, while the neighboring Zn/Sn atoms provide additional electron density through vacancy-induced charge redistribution. This dual-site coordination promotes electron filling into the O–O antibonding state, thereby weakening the O–O bond and facilitating subsequent ROSs generation. Additionally, ZHS-P-OVs also exhibit a strong adsorption affinity for  $C_7H_8$  ( $-2.00$  eV), with localized electron accumulation between P/OVs and molecular  $C_7H_8$  [51, 52]. Given that  $O_2$ ,  $H_2O$ , and  $C_7H_8$  coexist during the actual photocatalytic reaction process, we simulated the competitive adsorption of various small molecules. The results reveal that under competitive adsorption conditions, ZHS-P-OVs has the strongest co-adsorption energy ( $-3.53$  eV), attributable to its spatially differentiated active sites: Surface-exposed P preferentially anchors  $C_7H_8$ , while OV effectively captures  $O_2$  molecules. This dual-site architecture not only alleviates steric constraints from multi-molecular interactions but also facilitates targeted activation of reactants [53]. The synergistic interplay of P doping and OV establishes a high-flux electron transfer channel between the photocatalyst and adsorbates, which is proposed as the mechanistic origin of the enhanced photocatalytic activity.

According to previous reports [51, 52, 54], the adsorption and electron transfer behavior of  $H_2O$  and  $O_2$  over photocatalysts significantly contribute to the photocatalytic removal of VOCs. To gain an in-depth understanding, *in situ* DRIFTS experiments were conducted to observe the behavior of individual  $O_2$  and  $H_2O$  under irradiation. Initially, the reaction chamber was vacuum-treated for

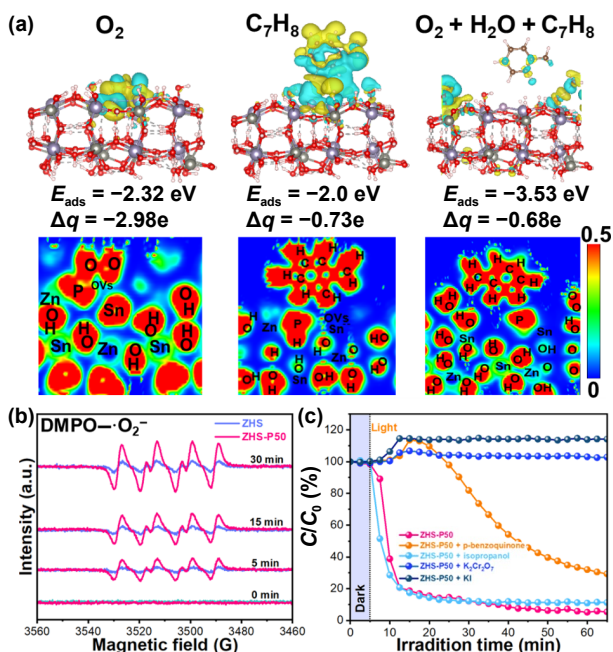
30 min to clean the sample surfaces, followed by the introduction of  $H_2O$  vapor under light. The adsorption peaks of  $H_2O$  ( $3000$ – $3600$   $cm^{-1}$ ) show no significant differences between ZHS and ZHS-P50 [55], implying that P doping and OV have minimal effect on  $H_2O$  absorption (Fig. S12 in the ESM). However, when  $O_2$  replaced  $H_2O$  in the reactor, the band at  $1610$   $cm^{-1}$  was observed over ZHS and ZHS-P50 (Fig. S13 in the ESM), which could be ascribed to the absorption of  $O_2$  [56]. More importantly, it can be found that the consumption of molecular  $O_2$  occurs in ZHS-P50 rather than bare ZHS. We can tell that  $O_2$  is more prone to O–O bond cleavage over ZHS-P50. In addition, the reduction ability of  $e^-$  enables the conversion of adsorbed  $O_2$  on the catalyst surface into  $\cdot O_2^-$  species, which is crucial for activating VOCs during the reaction.

According to Fig. 4(b) and Fig. S14 in the ESM, no EPR signals were detected in either sample under dark conditions. Upon irradiation, both ZHS and ZHS-P50 show typical 6 fold peak for 5,5-dimethyl-1-pyrroline N-oxide (DMPO)– $O_2^-$  and quadruple peaks for DMPO–OH with the relative intensities of 1:2:2:1 (Fig. S14 in the ESM) [57]. Notably, the intensity signals of the  $\cdot OH$  and  $\cdot O_2^-$  species in ZHS-P50 are greatly higher than those in ZHS, indicating the strong redox capacity in ZHS-P50. Free radical trapping experiments were further implemented to distinguish the dominant reactive species participating in photocatalytic  $C_7H_8$  degradation [30]. As presented in Fig. 4(c), the addition of p-benzoquinone (an  $\cdot O_2^-$  scavenger) partially suppresses the  $C_7H_8$  removal efficiency, which confirms that  $\cdot O_2^-$  serves as the primary active radical driving the degradation reaction. Potassium dichromate ( $K_2Cr_2O_7$ ) was introduced to trap photogenerated  $e^-$ , while potassium iodide (KI) was adopted as the hole ( $h^+$ ) scavenger. Significant decline in photocatalytic activity was observed after adding either scavenger, proving that both electrons and holes make vital contributions to  $C_7H_8$  oxidation. Besides, the introduction of isopropyl alcohol ( $\cdot OH$  scavenger) only slightly weakens the catalytic performance, which suggests that  $\cdot OH$  radicals play an auxiliary minor role in this photocatalytic system.

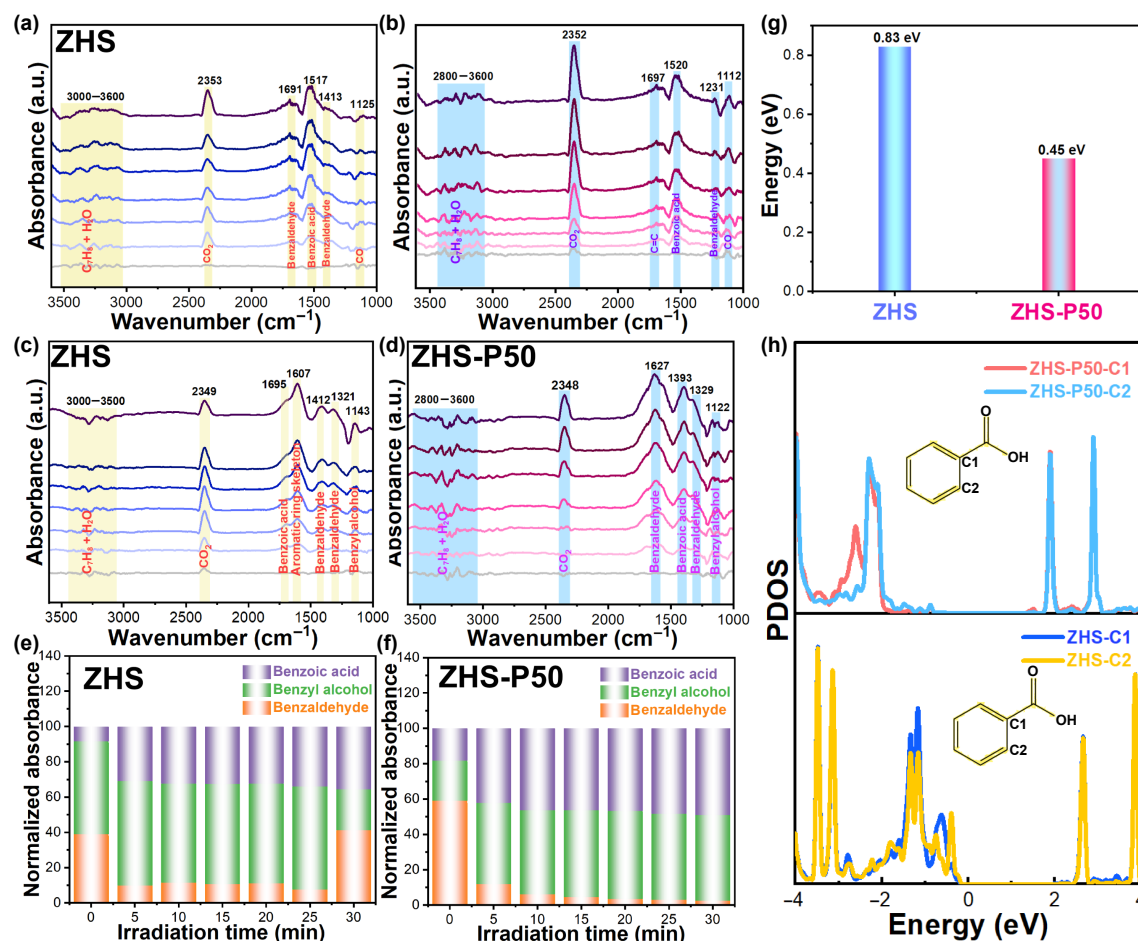
### 3.5 Mechanisms of photocatalytic $C_7H_8$ degradation

To get insights into the different reaction mechanisms over ZHS and ZHS-P50 during photooxidation, *in situ* DRIFTS experiments were applied to dynamically monitor the intermediates. The observed infrared (IR) band attributions are shown in Table S3 in the ESM. For bare ZHS (Fig. 5(a)), the detectable infrared bands include characteristic peaks for  $C_7H_8$  and  $H_2O$  ( $3000$ – $3600$   $cm^{-1}$ ), vibrational peaks for C–C bonds ( $1410$   $cm^{-1}$ ), signals for benzaldehyde ( $1413$  and  $1691$   $cm^{-1}$ ), a gradually decreased  $CO_2$  peak at  $2353$   $cm^{-1}$ , and weak CO peaks at  $1125$   $cm^{-1}$ .

Now let's focus on the situation of ZHS-P50 (Fig. 5(b)), the IR spectra give characteristic peaks belonging to the vibration of the C–H bond of gaseous  $C_7H_8$  and  $H_2O$  ( $2800$ – $3600$   $cm^{-1}$ ), C=O stretching vibration ( $1679$   $cm^{-1}$ ), benzaldehyde ( $1168$  and  $1231$   $cm^{-1}$ ), benzoate species ( $1520$   $cm^{-1}$ ),  $CO_2$  ( $2352$   $cm^{-1}$ ), and CO ( $1112$   $cm^{-1}$ ). As depicted in Figs. 5(c) and 5(d), multiple reaction intermediates are detected upon irradiation. For ZHS (Fig. 5(c)), the peaks can be well assigned to  $CO_2$  ( $2349$   $cm^{-1}$ ), benzoic acid ( $1695$   $cm^{-1}$ ), aromatic ring skeleton ( $1607$   $cm^{-1}$ ), benzaldehyde ( $1321$  and  $1412$   $cm^{-1}$ ), and benzyl alcohol ( $1143$   $cm^{-1}$ ). For ZHS-P50 (Fig. 5(d)), the spectra reveal stretching vibrations of alkoxide species ( $1122$   $cm^{-1}$ ), benzaldehyde ( $1329$  and  $1627$   $cm^{-1}$ ), benzoic acid ( $1393$   $cm^{-1}$ ), and  $CO_2$  ( $2348$   $cm^{-1}$ ). As the photocatalytic reaction proceeds, the  $CO_2$  peak intensity over pristine ZHS first



**Figure 4** (a) The spatial charge density and ELF of small molecules. (b) EPR spectra of DMPO– $O_2^-$ . (c) Trapping experiment of active radical over ZHS-P50.



**Figure 5** *In situ* DRIFTS spectra of photocatalytic  $C_7H_8$  reaction in dark and under irradiation for ((a) and (c)) ZHS and ((b) and (d)) ZHS-P50. Corresponding relative intensity of products on (e) ZHS and (f) ZHS-P50 during reaction process. (g) The energy barrier of  $C_7H_8O_2$  ring-opening and (h) the PDOS results.

risers and then declines. By comparison, a continuous growth of  $CO_2$  signal is detected on ZHS-P50 throughout the reaction, demonstrating the remarkably enhanced mineralization capacity of ZHS-P50 for  $C_7H_8$  photooxidation [58]. Notably, the accumulation of benzoic acid is detected at  $1695\text{ cm}^{-1}$  for ZHS and  $1393\text{ cm}^{-1}$  for ZHS-P50, highlighting its role as a crucial intermediate in the  $C_7H_8$  mineralization process. By normalizing the intensity of infrared peaks during the reaction process, we further investigated the selectivity of intermediate products [59]. The relative proportions of benzoic acid on ZHS-P50 are shown in Figs. 5(e) and 5(f). After 1 h of reaction, the yield of benzoic acid on ZHS-P50 is 49%, significantly higher than the 36% yield observed on ZHS. This result is in good line with the enhanced performance of photocatalytic  $C_7H_8$  oxidation, which means a more favorable conversion to the ring-opened byproducts of  $C_7H_8$ .

Afterward, as a crucial product, the formation of benzoic acid emerges as a key intermediate in the ring-opening of  $C_7H_8$ , underscoring its importance in the photocatalytic reaction [60]. To understand this process from a thermodynamic perspective, we calculated the energy barriers associated with the formation of benzoic acid. Specifically, the ring-opening of benzoic acid exhibits a lower energy barrier of  $0.45\text{ eV}$  for ZHS-P50 as compared with  $0.83\text{ eV}$  for ZHS (Fig. 5(g)), suggesting that the reaction proceeds more easily over ZHS-P50. This lower barrier aligns with the partial DOS (PDOS) results [61], where the highly overlapping 2p orbitals of C1 and C2 (C1 and C2 denote the two carbon atoms involved in

the ring-opening process of  $C_7H_8$ ) indicate a strong covalent interaction, representing an obstacle to the ring-opening of  $C_7H_8$ . By comparison, the weakened C=C covalent bond strength observed in ZHS-P50 facilitates the ring-opening of benzoic acid (Fig. 5(h)) [62], which is in good accord with the analytical results in Fig. 2(i). As such, these computational results prove the powerful advantage of P doping and OV in ZHS-P50, which synergistically promote the overall kinetics of the  $C_7H_8$  ring-opening process [63]. In addition, supplementary gas chromatography-mass spectrometry (GC-MS) measurements were performed on the reactor outlet gas (Fig. S15 in the ESM). Only fully mineralized products ( $CO_2$  and  $H_2O$ ) and trace unreacted  $C_7H_8$  are detected throughout the reaction process, while no characteristic signals of benzene, formaldehyde, formic acid, or other toxic low-molecular-weight intermediates are observed, which further corroborates the deep mineralization of  $C_7H_8$  in this photocatalytic system.

## 4 Conclusions

In this study, a ZHS-P50 was successfully synthesized, enabling efficient photocatalytic degradation of  $C_7H_8$ . The introduction of P dopants effectively triggered a self-defect modulation process that optimized OV concentrations, thereby enhancing charge carrier separation and transfer. Combined experimental and DFT calculations revealed that the synergistic effect between P doping and OV facilitated  $O_2$  activation, reduced the energy barrier of the rate-determining ring-opening step, and accelerated deep

mineralization of aromatic intermediates to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Consequently, ZHS-P50 achieved a high  $\text{C}_7\text{H}_8$  removal efficiency of 95%. This work provides new insights into defect-dopant interactions in perovskite-type hydroxides and establishes a rational strategy for designing advanced photocatalysts toward efficient and sustainable VOCs abatement.

**Electronic Supplementary Material:** Supplementary material (Raman spectroscopy measurements, SEM images, and BET surface area analysis) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909053>.

## Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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## Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

## Author contribution statement

Y. H. L.: Investigation, experimental design, data curation, software, writing manuscripts. W. H.: Formal analysis, data curation, review. X. X. Z.: Data curation, formal analysis. Y. C. F.: Software, formal analysis. Z. Y. M.: Investigation, data curation. P. T.: Software, supervision, writing manuscripts, funding acquisition, resources. All the authors have approved the final manuscript.

## Use of AI statement

None.

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