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# Integrating N and F co-doped $TiO_2$ nanotubes with ZIF-8 as photoelectrode for enhanced photo-electrocatalytic degradation of sulfamethazine



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# HIGHLIGHTS

- ZIF-8/NF-TiO<sub>2</sub> photoanode was fabricated via electro-anodization and insitu growth.
- The photo-electrocatalytic activity was attributed to heterojunction and synergy.
- Light and bias potential improved the charge generation, separation and transfer.
- The synergistic factor in photo-electrocatalytic process was calculated to be 3.5.
- Sulfamethazine (SMZ) degradation mechanisms and pathway were investigated.

# ARTICLE INFO

Keywords: Zeolitic imidazolate frameworks (ZIFs) Sulfamethazine Photo-electrocatalysis Anatase Rutile

# GRAPHICAL ABSTRACT



# ABSTRACT

Traditional photoanodes decreased in mass transfer rate via coating powdered catalysts on conductive glass. In this work, we obtained a visible light-driven semiconductor- metal organic frameworks (MOFs) hybrid photoelectrode, which was constructed by electro-anodization and deposition growth process. The ZIF-8/NF-TiO<sub>2</sub> photoelectrode was based on hollow TiO<sub>2</sub> nanotubes, and ZIF-8 nanoparticles were deposited on the surface of the pyramid-shaped rutile TiO<sub>2</sub> substrate after N and F co-doping. Compared with unmodified anatase TiO<sub>2</sub>, the reaction rate of ZIF-8/NF-TiO<sub>2</sub> increased by 21.7 times, and the synergistic factor in the photo-electrocatalytic process could reach to 3.5. The porous structure of ZIF-8, the intrinsic band difference between anatase and rutile TiO<sub>2</sub> greatly improved light utilization, and promoted electron–hole separation. The electrode could be easily recycled and exhibit excellent repeatability, and the degradation efficiency almost unchanged after 8 cycles. Moreover, possible degradation pathways and photo-electrocatalytic degradation mechanisms of sulfamethazine were proposed. This progress could bring novel insights for the design of semiconductor-MOFs hybrid photo-electrocatalysts.

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#### 1. Introduction

Water pollution has gradually become a major environmental issue of global concern due to pharmaceuticals continue to be widely used and personal care products and beauty products continue to be increase demanded [1,2]. Antibiotic contamination caused by pharmaceuticals loss has become emerging issue in recent years because of solubility, durability and high toxicity [3–6]. Sulfa antibiotics are one of the widely used antibiotics [7], which was selected as a model antibiotic because of high toxicity and risk to develop resistance for natural populations bacteria [3].

Photocatalytic technology has garnered particular attention because of mild reaction conditions, fast reaction rate and easy operation [8–10]. However, the easy recombination of electrons and holes bring challenges to traditional photocatalytic technology [11]. Notably, doping modification and heterojunction are effective strategies to avoid the combination of electrons and holes. Cao et al. [12] reported a Codoped UiO-66 nanoparticle with high visible-light catalytic activity and adsorption property to remove tetracycline. Z-scheme AgI BiOBr samples were developed by Yu et al. to photodegrade ciprofloxacin with a removal efficiency of 90.9% in 60 min [13]. Although the results of the cited strategies were significant, it was still challenging to effectively recover and avoid the secondary pollution caused by loss of powder catalyst.

In view of the recombination of electrons and holes, researchers have used electrochemistry assisted photocatalysis to effectively solve this problem. Photo-electrocatalysis (PEC) generated a potential gradient inside the photoelectrode by applying an anodic bias which could force the photogenerated electrons to move in the direction of the counter electrode and separate the photogenerated holes [14,15]. PEC not only fully exerted the synergistic effect of photo and electricity, but also solved the problem that the powder catalyst was difficult to be effectively recovered, and improved the recycling efficiency of the catalyst. However, common photoanode is constructed by coating powdered catalysts on conductive glass to form a bulk electrode [16], which caused decrease in mass transfer rate and dispersion. Therefore, effectively improving the mass transfer process has become a further research direction of PEC. As a novel material, metal organic frameworks (MOFs) are considered as the guest because of porous and high specific surface area [17]. The zeolitic imidazolate frameworks (ZIFs) could be considered for the construction of photoanodes because of the milder synthesis conditions, the chemical stability and easy to be loaded [18]. Meanwhile, TiO<sub>2</sub> nanotubes (TiO<sub>2</sub>-NTs) is considered as the matrix because of excellent electrical conductivity. Cardoso et al. have studied on efficient Photo-electrocatalytic reduction of CO2 by ZIF-8/ TiO<sub>2</sub>-NTs, the cooperative synergism between ZIF-8 and TiO<sub>2</sub> might enhance the photo-electrocatalytic performance of the photoanode [18]. However, pure  $TiO_2$  is a typical wide bandgap semiconductor with a band gap energy of 3.2 eV, and could only absorb ultraviolet light [16,19,20]. For TiO<sub>2</sub>, N-doping is considered to be one of the methods to effectively shorten the band gap and expand the absorb wavelength to visible light [21]. However, the oxidative power of photogenerated holes is relatively low, which caused by the mixed gap composed of N 2p and O 2p above the valence band (VB). Interestingly, Barndők et al. observed that introducing F ions into N-TiO<sub>2</sub> could effectively settle this shortcoming and shift the conduction band (CB) [22].

Based on the above researches, we constructed a composite photoanode with N and F co-doped  $TiO_2$ -NTs as the matrix and ZIF-8 as the guest. Considering the effect of  $TiO_2$  crystal facet on photoelectron transfer, this study selected pyramidal NF-TiO<sub>2</sub> film with dominant exposure of (1 0 1) crystal plane as the deposition surface for ZIF-8 insitu growth. Under visible light irradiation, PEC was carried out with sulfamethazine (SMZ) as a target contaminant. Meanwhile, the morphological structure, optical performance, photoelectric performance and PEC activity of the prepared ZIF-8/NF-TiO<sub>2</sub> film electrode were



Fig. 1. XRD patterns of film electrodes TiO<sub>2</sub>, ZIF-8/TiO<sub>2</sub>, NF-TiO<sub>2</sub>, ZIF-8/NF-TiO<sub>2</sub>.

tested, and relevant factors (solution pH, electrolyte concentration, etc.) were intensively studied. In addition, the possible degradation mechanism of SMZ under PEC conditions was proposed. The new strategy reported here which solved the recycling problem and simultaneously reduced the photo-generated carrier recombination rate could enrich the method for designing novel semiconductor-MOFs hybrid photo-electrocatalysts.

## 2. Experimental section

The materials, preparation of  $ZIF-8/NF-TiO_2$ , characterization of the photoelectrodes, photoelectrochemical measurements and the photoelectrocatalytic activity experiment process were shown in Supporting Information.

#### 3. Results and discussion

#### 3.1. Characterization of the photoelectrodes

XRD of the prepared film electrodes was shown in Fig. 1. Obviously, a main diffraction peak at 25.3° could be observed in all the resultant samples, which was well indexed to anatase (1 0 1) facets (JCPDS No. 21-1272). The peak was relatively stronger, indicating that the synthesized TiO<sub>2</sub> with high degree of crystallinity [23]. When N and F was co-doped into TiO2-NTs, the appeared diffraction peaks behaved similarly as that of rutile (1 1 0). Consistent with the previous studies [24], the formation of rutile (1 1 0) could be seen as the signal of anatase-rutile heterojunction, which was formed by calcining TiO<sub>2</sub>-NTs under the NH<sub>4</sub>F. As for ZIF-8, peaks at 7.36° was ascribed to the (0 1 1) crystal planes of ZIF-8 [25], which verified the successful incorporation of ZIF-8. According to the results, we could clear that anatase-rutile heterojunction was formed, and ZIF-8 was successful incorporated into the film electrode. Notably, the characteristic diffraction peaks of ZIF-8 were relatively weak, which might be ascribed to the limited load. In addition, no additional peaks for ZIF-8 were obtained because of the low content and high dispersion.

The morphology and microstructure of film electrodes were characterized by SEM. The elemental mapping (Fig. S1) and energy spectrum distribution (Fig. S2) have been performed for C, O, N, F, Ti and Zn, the SEM images were displayed in Fig. 2. The TiO<sub>2</sub>-NTs displayed relatively uniform hollow tubulars with diameters changing from 40 to 50 nm and an average thickness of 20 nm. The loading of ZIF-8 on TiO<sub>2</sub>-NTs (Fig. 2a) resulted in the agglomerates of nanoparticles formed by nucleation and growth, with an average size of 15–30 nm. And ZIF-8 deposited on the surface or the interior of the TiO<sub>2</sub>-NTs, without



Fig. 2. SEM images of (a) ZIF-8/TiO<sub>2</sub>, (b) NF-TiO<sub>2</sub>, (c) and (d) ZIF-8/NF-TiO<sub>2</sub>; (e)(f) TEM and (g) HRTEM of ZIF-8/NF-TiO<sub>2</sub>.

completely blocking of the nanotubes. Interestingly, when TiO<sub>2</sub>-NTs was calcined in the presence of NH<sub>4</sub>F, the tubular structure dramatically changed into particle-shape or pyramid-shape (Fig. 2b), respectively. It is worth mentioning that no particle-shape or pyramid-shape was observed when pure Ti foil under the same calcination conditions or calcining the TiO<sub>2</sub>-NTs in the presence of NH<sub>4</sub>Cl [24]. Accordingly, we speculated the use of tubular structures as precursors was essential for the formation of particle-shape or pyramid-shape NF-TiO<sub>2</sub>. And the reason why the morphology of NF-TiO<sub>2</sub> so different from TiO<sub>2</sub>-NTs was the etching of HF. When TiO<sub>2</sub>-NTs was calcined at 450°C, the nanotubes would be simultaneously etched by HF and doped by NH<sub>3</sub> which originated from the decomposition of NH<sub>4</sub>F. Finally, as shown in Fig. 2c and d, smaller ZIF-8 nanoparticles uniformly deposited and dispersed on the surface of NF-TiO<sub>2</sub>.

The TEM measurement was introduced to further study the internal structure of ZIF-8/NF-TiO<sub>2</sub>. Obvious particles in Fig. 2e suggested the existence of ZIF-8-NPs, and the image in Fig. 2f suggested that ZIF-8-NPs had closely attached on NF-TiO<sub>2</sub>. Fast Fourier transform (FFT) were calculated to obtain the lattice structure (Fig. 2g). The lattice fringe spacings were 0.35 nm and 0.32 nm, which were in coincidence with

the (1 0 1) planes of the anatase structure  $\text{TiO}_2$  and the (1 1 0) planes of the rutile structure  $\text{TiO}_2$ , respectively [25]. All analysis mentioned above performed that ZIF-8-NPs successfully decorated on the surface of ZIF-8/NF-TiO<sub>2</sub> with good dispersion, which confirmed the XRD results.

The composition and valence state of ZIF-8/NF-TiO<sub>2</sub> were further analyzed by XPS. The survey spectrum results presented that the ZIF-8/ NF-TiO<sub>2</sub> was mainly made up of carbon, titanium, zinc, oxygen, nitrogen and fluorine. The signals of C 1s, Ti 2p, Zn 2p, O 1s, N 1s and F 1s could be observed in Fig. 3a, and the high resolution XPS spectrum for each element was also recorded. For C 1s (Fig. 3b), the spectrum could be divided into peaks C=O (288.2 eV), C-O (285.4 eV), C-C (284.8 eV) and C=C (284.4 eV) [26]. And in the Ti 2p XPS spectrum (Fig. 3c), the main fitting peaks at 464.2 eV and 458.3 eV were correspond to Ti  $2p_{1/2}$  and Ti  $2p_{3/2}$ , respectively [27]. Additionally, the Zn 2p fitting peaks situated at 1044.9 eV and 1021.7 eV (Fig. 3d) were correspond to Zn  $2p_{1/2}$  and Zn  $2p_{3/2}$ , respectively [28]. The O 1s XPS spectrum was fitted by three peaks (Fig. 3e), which were 532.0 eV, 530.1 eV and 529.4 eV. The energy peak located at 532.0 eV corresponded to the surface-adsorbed oxygen type (O–H) [29]. The energy



Fig. 3. XPS spectrum of ZIF-8/NF-TiO<sub>2</sub> (a) survey spectra, (b) high resolution C1s, (c) high resolution Ti 2p, (d) high resolution Zn 2p, (e) high resolution O 1s, (f) high resolution N 1s.

peak located at 530.1 eV corresponded to the Ti-O bond, which was attributed to the formation of TiO<sub>2</sub>-NTs [30]. The energy peak located at 529.4 eV corresponded to the Zn-O bond, which was attributed to the formation of ZIF-8 [31]. Moreover, the N 1s region consists of three peaks (Fig. 3f). The main fitting peaks at 400.1 eV, 399.6 eV and 398.7 eV were attributed to N-C bond from imidazole ring in ZIF-8, N-Ti-O bond and N=C bond [32]. The source of N1s was owing to two aspects. The successful loading of ZIF-8-NPs and the co-doping of N-F could both introduce N to film electrode. Of note, the high resolution XPS spectrum of N1s in ZIF-8/TiO<sub>2</sub>-NTs was almost undetectable (Fig. S3a), which might due to the low content of N. While the signal of N1s in ZIF-8/NF-TiO<sub>2</sub> was obviously, and the N 1s of ZIF-8/NF-TiO<sub>2</sub> was

much higher than that of ZIF-8/TiO<sub>2</sub>-NTs (Fig. S3b). Bearing these in mind, we believed that the formation of N-Ti-O bond was mainly attributed to part of the O atom in TiO<sub>2</sub>-NTs replaced by N atom from NH<sub>4</sub>F. The F 1s peak located at 684.7 eV (illustration of Fig. 3a) was ascribed to the incorporation of F in TiO<sub>2</sub>-NTs [33]. The atomic ratio of N and F to Ti by XPS were calculated to be 14.6% and 15.8%, respectively. According to the XPS results, N and F were both incorporated into the bulk phase of the TiO<sub>2</sub> after calcination at 450 °C. The loading of ZIF-8 on TiO<sub>2</sub> doped with both N and F was confirmed to be successful.

The band gap energies  $(E_g)$  of the film electrodes were analyzed via UV–vis diffuse reflectance spectroscopy (DRS). All electrodes had the



Fig. 4. (a) UV-vis adsorption spectra of samples. (b) Plots of  $(\alpha h\nu)^2$  vs photon energy for samples.

steep absorption edges (Fig. 4a), implying that the formation of absorption edges was the intrinsic transition of the nanomaterials rather than a transition from impurity levels. The absorption edges were in order: ZIF-8/NF-TiO<sub>2</sub> > NF-TiO<sub>2</sub> > ZIF-8/TiO<sub>2</sub>-NTs > TiO<sub>2</sub>-NTs, the absorption edge of ZIF-8/NF-TiO<sub>2</sub> was 553 nm. The band gap energy was evaluated by the transformational Tauc plots, according to the Kubellka-Munk equation [34], the E<sub>g</sub> values were estimated to be 2.88 eV, 2.96 eV, 3.15 eV and 3.23 eV for ZIF-8/NF-TiO<sub>2</sub>, NF-TiO<sub>2</sub>, ZIF-8/TiO<sub>2</sub>-NTs and TiO<sub>2</sub>-NTs, respectively (Fig. 4b).

Compared with the TiO<sub>2</sub>-NTs, the absorption edge of ZIF-8/TiO<sub>2</sub>-NTs showed somewhat red-shift because the porous structure of ZIF-8 could effective use the multiple reflection of incident light, indicated that the diversification of the options for photoelectrode was interaction between the TiO<sub>2</sub>-NTs and ZIF-8 [18]. Notably, compared with TiO<sub>2</sub>-NTs and ZIF-8/TiO<sub>2</sub>-NTs, the absorption edges of NF-TiO<sub>2</sub> and ZIF-8/NF-TiO<sub>2</sub> were red-shifted obviously, and the absorption band even extended to the visible range of 500–600 nm, which was consistent with the study that the absorption edges of TiO<sub>2</sub> (TiO<sub>2</sub>-NPs) after N,F co-doping was extended to the visible region [22]. The broader absorption lead to more carriers utilized by photo-electrocatalyst, and generate more active radicals and better PEC performance [35]. The improved visible light response was considered to enhance the PEC activity of ZIF-8/NF-TiO<sub>2</sub> towards SMZ molecules.

In general, the PEC activity positively relates to light harvesting ability, charge separation and the recombination rate of photo-excited electrons and holes [36]. To investigate the photophysical behavior of the photoelectrode, the PL spectra of TiO2-NTs, ZIF-8/TiO2-NTs, NF-TiO<sub>2</sub> and ZIF-8/NF-TiO<sub>2</sub> were recorded with excitation wavelength of 325 nm. It could be seen that the broad luminescence peak of TiO<sub>2</sub> was between 450 nm and 480 nm, which were dependent on the excitation luminescence peak that caused by surface states and defects [37]. The undoped and doped TiO<sub>2</sub>-NTs showed similar emission peak pattern, demonstrating that N and F did not give rise to new PL phenomena. However, the intensity of PL signals was greatly decreased. As shown in Fig. 5, the integrated PL intensity was confirmed to the order: TiO<sub>2</sub>-NTs > ZIF-8/TiO<sub>2</sub>-NTs > NF-TiO<sub>2</sub> > ZIF-8/NF-TiO<sub>2</sub>. The excitonic PL intensity of ZIF-8/TiO<sub>2</sub>-NTs was lower than that of TiO<sub>2</sub>-NTs, which might be due to the reduction of defect and indirect recombination efficiency caused by Zn and N from ZIF-8 [38,39]. ZIF-8/NF-TiO2 exhibited the lowest photoluminescence intensity, which might be attributed to that N and F filled the vacancies, reduced the absorption of electrons by oxygen vacancies, promoted the transition of electrons from VB to CB, and reduced the intensity of the photoluminescence peak caused by the bound excitons [40]. Meanwhile, external circuit transmission improved the charge separation. It has been generally understood that the PEC activity increased when PL intensity (or the



Fig. 5. Steady-state photoluminescence spectra of the as-prepared electrodes.

recombination of  $e^-$  and  $h^+$ ) decreased [41]. Therefore, ZIF-8/NF-TiO<sub>2</sub> exhibited the most positive PEC activity.

#### 3.2. Photoelectrochemical characterizations

To analyze the separation rate of photogenerated carriers, the transient photocurrent densities of photoanodes in 0.5 M Na<sub>2</sub>SO<sub>4</sub> were characterized under visible light irradiation. As illustrated in Fig. 6a, the photocurrent densities of photoanodes presented a well-correlated variation with the on/off cycles. Almost none photocurrent was observed on the TiO<sub>2</sub>-NTs, while obvious photocurrent response could be observed when ZIF-8 was loaded onto TiO2-NTs, suggesting that ZIF-8 was an effective visible light-sensitizer. ZIF-8/NF-TiO<sub>2</sub> performed the highest photocurrent density, which was approximate 4 times and 2 times higher than that of ZIF-8/TiO<sub>2</sub>-NTs and NF-TiO<sub>2</sub>, implying that the photogenerated electrons of ZIF-8/NF-TiO<sub>2</sub> flowed anode to the cathode were the most. Therefore, we had reason to think that the loading of ZIF-8 and the doping of N and F played vital influences on the generation, separation, transportation of photogenerated electrons [42]. The EIS measurement provided information on the interfacial charge transfer behaviors. In the EIS Nyquist plots, the smaller the radius of the circle, the lower the charge transfer resistance. As shown in Fig. 6b, the smallest radius was observed on ZIF-8/NF-TiO<sub>2</sub>, which demonstrated that the interfacial layer resistance on ZIF-8/NF-TiO2 was the lowest.

The Mott-Schottky plot tested the relationship of impedance with potential at a fixed frequency. As shown in Fig. 6c, NF-TiO<sub>2</sub> showed n-



**Fig. 6.** (a) Photocurrent transient response curves. (b) EIS Nyquist plots with frequency range from  $10^{0}$  Hz to  $10^{5}$  Hz. (c) Mott-Schottky plots and cyclic voltammetry of ZIF-8/NF-TiO<sub>2</sub>. (d) Linear sweep voltammograms of the as-prepared electrodes. Photocurrent density of (e) TiO<sub>2</sub> and (f) ZIF-8/NF-TiO<sub>2</sub> under visible light irradiation without and with 0.5 M H<sub>2</sub>O<sub>2</sub>. Experimental conditions: Na<sub>2</sub>SO<sub>4</sub> concentration = 0.5 M, pH = 3.5, initial SMZ concentration = 10 mg L<sup>-1</sup>.

type semiconductor characteristic, and the flat band potential was -0.69 V. The semiconductor properties of ZIF-8/NF-TiO<sub>2</sub> remained ntype, while the flat band potential was negatively shifted by 0.1 V. When potential higher than flat band, h<sup>+</sup> was driven to the electrode surface [43] and 'OH were generated from water oxidation [44]. The cyclic voltammetry curve showed that the electrode was not oxidized at a voltage of 2 V. When a positive bias potential was applied (2 V vs Ag/ AgCl), ZIF-8/NF-TiO<sub>2</sub> had a larger potential difference than NF-TiO<sub>2</sub>. The larger bending of the CB in ZIF-8/NF-TiO<sub>2</sub> caused greater charge separation (e<sup>-</sup>/h<sup>+</sup>). The Mott-Schottky measurement confirmed the improvement of the interfacial electron transfer kinetics for ZIF-8/NF-TiO<sub>2</sub>, which improved PEC efficiency of SMZ. The increased photocurrent of ZIF-8/NF-TiO<sub>2</sub> in the LSV diagram also confirmed the point (Fig. 6d). Apart from electronic transfer process, the injection efficiencies of photogenerated holes to the electrolyte also played a pivotal role in PEC degradation. Since photogenerated holes could recombine with in electrons in the bulk and surface traps, the yield of photogenerated holes reaching the electrode/electrolyte interface and injected into the electrolyte tends to be lower than the photocurrent density produced by the photon-absorbing light energy [45]. We could interpret this part that was annihilated by recombination as composite loss, and called the ratio of the two yields as surface transfer efficiency ( $\eta_i$ ) [46]. The higher the surface charge transfer efficiency, the more favorable the electron injection solution for reaction. In order to evaluate the photo-electric utilization performance, we utilized H<sub>2</sub>O<sub>2</sub> as a hole scavenger to further quantify the  $\eta_i$  in the PEC system. Therefore,



**Fig. 7.** (a) PEC degradation dynamics and (b) pseudo-first-order kinetic curves of SMZ using different photoanodes; (c) comparison of SMZ degradation dynamics and (d) pseudo-first-order kinetic curves using ZIF-8/NF-TiO<sub>2</sub> electrode under different processes. Experimental conditions:  $Na_2SO_4$  concentration = 0.5 M, pH = 3.5, initial SMZ concentration = 10 mg L<sup>-1</sup>.

the photocurrent density generated by the PEC could be described by the following equation:

$$J_P = J_{abs} \times \eta_{sep} \times \eta_t \tag{1}$$

where  $J_p$  is the photocurrent density in electrolyte,  $J_{abs}$  is photocurrent density produced by the photon-absorbing light energy,  $\eta_{sep}$  is the yield of the holes that reach the electrode/electrolyte interface,  $\eta_t$  is the yield of holes that have reached the electrode/electrolyte interface and injected into the electrolyte.

In the presence of H<sub>2</sub>O<sub>2</sub>, the recombination in surface traps was completely suppressed ( $\eta_t = 1$ ) [47], and the photocurrent density in this limit was expressed as Eq. (2):

$$J_P^{H_2O_2} = J_{abs} \times \eta_{sep} \tag{2}$$

Surface transfer efficiency  $(\eta_t)$  could be calculated based on equations (1) and (2) when probed with the same photoanode.

Thus, we have experimentally obtained the  $\eta_t$  of TiO<sub>2</sub> (Fig. 6e) was 5.3%. Once combined with ZIF-8, the charge injection efficiency of ZIF-8/NF-TiO<sub>2</sub> (Fig. 6f) was significantly improved, reaching 58.3% at a potential of 2.0 V. The higher  $\eta_t$  of ZIF-8/NF-TiO<sub>2</sub> indicated that the inject efficiency of the electrons into solution was more excellent. Compared with TiO<sub>2</sub>-NTs, the positive and negative photocurrent curve transient of ZIF-8/NF-TiO<sub>2</sub> disappeared, which demonstrated that h<sup>+</sup> reaching the electrode/electrolyte interface could effectively participate in the reaction, and no recombination occurred between the electron and photo-electrooxidized surface [45]. In summary, various photoelectrochemical characterizations of film electrodes were studied to analyze the electron transfer and interface transmission process from

multiple perspectives, and the results further supported the results of PL spectrum.

# 3.3. Photo-electrocatalysis activity

In the present study, the PEC performance of film electrodes was evaluated by the degradation of SMZ during 180 min in 0.5 mol L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>, and the adsorption performance were exhibited in Fig. S4. As shown in Fig. 7a, the removal efficiencies of TiO<sub>2</sub>-NTs, ZIF-8/TiO<sub>2</sub>-NTs, NF-TiO<sub>2</sub> and ZIF-8/NF-TiO<sub>2</sub> were 7.0%, 30.0%, 40.1% and 81.3%, respectively. Furthermore, sulfamethazine degradation compared to other PC, EC studies done on SMZ degradation were listed in Tab. S1. Around 7.0% degradation was observed in the presence of TiO<sub>2</sub> film electrode, which might be due to the combination of the presence of trace visible light and an oxidation effect by dissolved oxygen in the suspension. The degradation kinetics of SMZ was assessed by the following Eq. (3) [35]:

$$-\ln\left(\frac{C_t}{C_0}\right) = kt \tag{3}$$

After curve fitting (Fig. 7b), the plots of  $\ln(C_0/C_t)$  versus *t* were found to be a linear relationship, and the degradation of SMZ followed pseudo-first-order kinetics with the correlation of coefficient higher than 0.97. The pseudo-first-order rate constant on ZIF-8/NF-TiO<sub>2</sub> was calculated to be 0.0089 min<sup>-1</sup>, about 3.4 times and 5.6 times relative to NF-TiO<sub>2</sub> (k = 0.0026 min<sup>-1</sup>) and ZIF-8/TiO<sub>2</sub>-NTs (k = 0.0016 min<sup>-1</sup>), respectively.

The optimal ZIF-8/NF-TiO2 film electrode was also investigated in



Fig. 8. Effect of external potential on the PEC degradation (a) degradation dynamics, (b) estimated rates constants and E%; Effects of (c) initial pH, and (d) electrolyte concentration in degradation rates of SMZ. Experimental conditions: initial SMZ concentration = 10 mg L<sup>-1</sup>.

H



Fig. 9. Effect of coexisting anions (Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>) and humic acid on SMZ degradation by ZIF-8/NF-TiO<sub>2</sub>.

photocatalytic (PC) and electrocatalytic (EC) process. As shown in Fig. 7c and d, the removal efficiency for SMZ after 180 min reaction was 29.85% in EC process, while the value was only 9.98% in PC process. Excitingly, the removal efficiency of PEC process could reach 81.30%, which was nearly twice the sum of the both former processes. Therefore, a synergistic effect could be observed in the PEC process, and the synergistic factor (SF) was assessed to be 3.5:

$$SF = \frac{k_{PEC}}{k_{PC} + k_{EC}}$$
(4)

where  $k_{PEC}$ ,  $k_{PC}$  and  $k_{EC}$  represented the rate constants for SMZ degradation in the PEC, PC and EC processes, respectively [48].

Additionally, we carried comparative PEC experiments at different voltages (Fig. 8a and b) to further investigate the effect of applied potential on the photo-electrocatalytic activity. The extent of the electrochemical enhancement (E, %) was assessed by the following Eq. (5):

$$E = \frac{k_{PEC} - k_{PC}}{k_{PEC}} \times 100\%$$
<sup>(5)</sup>

The E value at 1.0 V was 42.0%, whereas it increased to 91.37% at 2.0 V. When the voltage varied to 3.0 V, the E value increased to 97.32%, showing that the enhancement trend obviously slowed down. Thus, 2.0 V was selected as operating voltage for the purpose of energy conservation.

Initial solution pH had vital influence on removal efficiency because of the SMZ ionization in aqueous solution [49,50]. Fig. 8c indicated that when pH varied from 2.0 to 3.5, the removal efficiency of SMZ increased, while the PEC activity decreased with the pH further increased. The highest removal efficiency of SMZ was observed at pH 3.5. The phenomenon could be explained as follows: (i) The nature of the target pollutant. The target pollutant carried an amino group and exhibited alkaline characteristics when exposed to water. Therefore, it was more conducive to degrade pollutants under acidic conditions; (ii) The change of the redox potential. The redox potential of SMZ always decreased with the increase of pH, and part of the photogenerated electrons generated under the photoelectric effect could be directly absorbed by SMZ, so the higher the pH, the lower the thermodynamic driving force; (iii) The oxidative ability of photoanode. The pH affected the VB potential of the photoanode. When the pH increased, the VB of the photoanode would shift to a more negative potential, which was



Fig. 10. (a) Long-time photocurrent decay curve; (b) Recycling tests; (c) Photocurrent transient response curves and (d) XRD patterns of ZIF-8/NF-TiO<sub>2</sub> before and after PEC process.

detrimental to the separation of  $e^-/h^+$ , resulting in reduced oxidizing power. Therefore, there was an optimal pH value for SMZ photo-electrocatalysis under acidic condition.

Na<sub>2</sub>SO<sub>4</sub> was used as electrolyte to maintain conductivity, and the concentration of Na2SO4 also had great impact on the degradation of SMZ. The results (Fig. 8d) showed that the concentration of Na<sub>2</sub>SO<sub>4</sub> could promote the degradation of target pollutants, while the promotion effect was obviously weakened when the concentration of Na<sub>2</sub>SO<sub>4</sub> was increased to 1.0 M. In addition to the controllable factors, the effect of the water microenvironment on degradation was expressed in Fig. 9. In general, there were humic acid (HA) and other anions coexisting with SMZ molecules in the actual wastewater, and HA was a typical dissolved organic matter in water which concentration ranged from 0 to  $30 \text{ mg} \text{L}^{-1}$ . Therefore, the decay of SMZ was investigated by the addition of inorganic anions such as  ${\rm Cl}^-$ ,  ${\rm CO_3}^{2-}$ ,  ${\rm PO_4}^{3-}$  and HA. NaCl, Na<sub>2</sub>CO<sub>3</sub> and Na<sub>3</sub>PO<sub>4</sub> were added to the SMZ solution to evaluate their effect on the PEC performance of the ZIF-8/NF-TiO<sub>2</sub> film electrode. As exhibited in Fig. 9, with the addition of  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{PO}_4^{3-}$  and HA, the degree of SMZ decay decreased as the strength increased, and the effectiveness in suppressing SMZ decay was HA  $PO_4^{3-} > CO_3^{2-} > Cl^-$ . The adverse impact of the above-mentioned anions and HA might be attributed to the scavenging of active radicals such as  $h^+$  and 'OH [51]. It could be seen from Eqs. (6) and (7) that  $PO_4^{3-}$  and  $CO_3^{2-}$  was converted to weaker selective radical  $PO_4^{2-}$ and  $CO_3^-$  by consuming, OH. The Cl<sup>-</sup> could react with the OH (Eqs. (8) and (9)) and h<sup>+</sup> (Eqs. (10)) to form <sup>·</sup>Cl, and the oxidizing power of 'Cl was stronger than 'PO<sub>4</sub><sup>2-</sup> and 'CO<sub>3</sub><sup>-</sup>. Meanwhile, because of the degradability, HA competed with SMZ for active radicals, and reduced the removal efficiency of SMZ [52]. The results also confirmed that h <sup>+</sup> and 'OH were closely related to the PEC process.

$$PO_4^{3-} + OH \to OH^- + PO_4^{2-}$$
 (6)

$$\text{CO}_3^{2-} + \text{OH} \to \text{OH}^- + \text{CO}_3^-$$
 (7)

 $Cl^- + OH \rightarrow HOCl^-$  (8)

$$HOCl^{-} + H^{+} \rightarrow Cl + H_{2}O$$
(9)

$$Cl^{-} + h^{+} \rightarrow Cl \tag{10}$$

Excellent electrodes should be outstanding in both stability and recyclability. As for the stability, long-time photocurrent decay curve of ZIF-8/NF-TiO<sub>2</sub> film electrode was continuously tested at 2 V (vs Ag/ AgCl). As displayed in the Fig. 10a, the photocurrent curve was no obvious downtrend, indicating that the photoelectrode had excellent light stability. As for the repeatability, ZIF-8/NF-TiO<sub>2</sub> film electrode run 8 cycles under the same conditions. The removal efficiency decreased by only 7.8% after 8 cycles (Fig. 10b). Compared with powder catalyst, ZIF-8/NF-TiO<sub>2</sub> film electrode avoided the problem of reduced recovery efficiency, and exhibited more reproducible in SMZ degradation. The synchronous decrease in photocurrent density with removal efficiency was shown in Fig. 10c. The XRD pattern of ZIF-8/NF-TiO<sub>2</sub> film electrode after 8 cycles exhibited no significant change compared to the XRD pattern of fresh film electrode (Fig. 10d). Moreover, the SEM image (Fig. S5) after cycle displayed no change except for the slight agglomeration of the ZIF-8 particles, further indicating that the prepared film electrode was stable.

#### 3.4. Catalytic mechanism

To analyze the possible PEC mechanism of SMZ, free radical quenching studies were conducted to assess the main active species by using different scavengers. In the free radical quenching study, three



Fig. 11. Effects of different radical scavengers on degradation of SMZ by ZIF-8/NF-TiO<sub>2</sub> (a and b); ESR spectra of (c) DMPO-  $O_1^-$  adduct and (d) DMPO-  $O_2^-$  adduct for ZIF-8/NF-TiO<sub>2</sub> under visible light irradiation ( $\lambda > 420$  nm).



Fig. 12. Proposed mechanisms in ZIF-8/NF-TiO<sub>2</sub>.

radical scavengers TBA, BQ, and EDTA-2Na were used to capture 'OH,  $O_2^-$ , an h<sup>+</sup>, respectively [12]. It could be seen from Fig. 11a and b that after adding excess TBA and BQ, the removal efficiency of SMZ was obviously suppressed, particularly in TBA, the removal efficiency of SMZ decreased from 81.3% to 22.5% within 180 min. Therefore, OH and  $O_2^-$  species were the effective active species which were responsible for the SMZ degradation, h<sup>+</sup> also acted as an assistant. The

result of the capture experiment was further verified by ESR. Fig. 11c and d displayed the ESR signals of DMPO-'OH and DMPO-' $O_2^-$ . No obvious characteristic peaks appeared in the dark, while the signals of DMPO-'OH and DMPO-' $O_2^-$  adducts were detected after 10 min. The results revealed that ZIF-8/NF-TiO<sub>2</sub> could be excited by visible light irradiation to generate 'OH and ' $O_2^-$  species.

Based on the above results, such as the enhancement of



Fig. 13. Proposed transformation pathways of SMZ degradation.

photocurrent, the expansion of absorption edge and the formation of special chemical bonds, combined the previous literature [25], the possible degradation mechanism of SMZ in PEC process was proposed. The synergistic effect between NF-TiO2 and ZIF-8 lead to the enhancement of the PEC activity of ZIF-8/NF-TiO2. The hollow tubular structure of TiO2-NTs could be effectively used as a precursor for the formation of pyramid-shape NF-TiO2. After doping with N and F, the wider absorption edge (to 554 nm) could promote the excitation of photogenerated  $e^{-}/h^{+}$  pairs. Meanwhile, the heterojunction structure between rutile phase and anatase would facilitate the separation of e<sup>-/</sup>  $h^+$  pairs [24]. After rutile phase and anatase contact, the higher Fermi energy of anatase contact than rutile phase caused the energy bands of anatase to bend upward and rutile phase to bend downward toward the interface to reach electrical equilibrium. As shown in Fig. 12, ZIF-8 acts as a cocatalyst, and formed a heterojunction-like structure with NF-TiO2. In addition, the N-Ti-O bond formed by the contact of ZIF-8 with  $TiO_2$  contributed to the transfer of e<sup>-</sup> generated by ZIF-8 to the surface of NF-TiO2. On the other hand, other chemical bonding structures formed by the contact between ZIF-8 and NF-TiO2 could promote effective separation of photogenerated  $e^{-}/h^{+}$  pairs [39].

Therefore, the possible mechanism was proposed as follows. The rutile phase provided another passageway for the  $e^-/h^+$  transfer process. The  $e^-$  in the CB of ZIF-8 could overcome the interface barrier and further migrated to the CB of NF-TiO<sub>2</sub> with highly reductive (1 0 1) facets, which were opportunely transferred to the cathode by an external circuit. Electrons were further captured by O<sub>2</sub> in the solution to form 'O<sub>2</sub><sup>-</sup>. The h<sup>+</sup> in the VB of NF-TiO<sub>2</sub> would migrate to ZIF-8, which could directly oxidize contaminants into small molecules, and h<sup>+</sup>, 'O<sub>2</sub><sup>-</sup> and 'OH could further degrade SMZ into smaller intermediates or directly degrade to final products (CO<sub>2</sub> and H<sub>2</sub>O). Herein,  $e^-/h^+$  pairs

separation was significantly enhanced and recombination was appreciably suppressed, which leading to higher PEC activities.

#### 3.5. Degradation pathway of sulfamethazine by ZIF-8/NF-TiO<sub>2</sub>

To investigate the intermediates of SMZ, LC-MS was carried out to perform mass measurements after extraction with methanol. The LC patterns displayed that the intensity of SMZ peak gradually weaken with the prolongation of illumination time, while it could still be detected after 180 min due to incomplete mineralization. According to the chromatogram and mass spectrum, the product with m/z = 279 was correspond to the molecular weight of SMZ, five intermediates were identified, including N-(4,6-dimethylpyrimidin-2yl) benzene-1,4-diamine (m/z = 214), 4,6-dimethylpyrimidin-2ol (m/z = 124), 4-aminophenol (m/z = 109), mono-hydroxyl derivatives (m/z = 294) and SO<sub>2</sub> elimination-hydroxyl derivatives (m/z = 230). Based on the identified byproducts and the studies published previously [53,54], the possible three main degradation pathways of SMZ were proposed in Fig. 13.

During the PEC degradation process, the above five intermediates were mainly generated through three routes: the oxidation of h<sup>+</sup>, the attack of 'OH and direct hydroxylation under the photoelectric conditions. Product 1 (m/z = 214) appeared in both pathway 1 and pathway 2. The formation of product 1 was mainly the cleavage of S-N bond, and SO<sub>2</sub> elimination driven by 'OH. The SO<sub>2</sub> elimination led to the aminobenzene ring directly attach to the pyrimidine ring, which was frequently observed in the degradation of SMZ [7,35]. The pathway 1 was product 1 continuously attacked by 'OH, where C-N bond between two benzene rings was cleaved and formed to product 2 (m/z = 124) and product 3 (m/z = 109). The pathway 2 was mainly the oxidation of h<sup>+</sup>.

The product 4 (m/z = 230) was obtained by direct oxidation of product 1 with h<sup>+</sup>. Comparing pathway 1 and pathway 2, the ability to oxidize pollutants of h<sup>+</sup> was weaker than 'OH [55]. The pathway 3 was mainly hydroxylation process, which was typical reaction responsible for SMZ degradation. Different structures of P5 (m/z = 294) were obtained by attaching the hydroxyl to different positions of SMZ [54], including the direct hydroxylation of the dimethyl pyrimidine group and the benzene ring. Subsequently, P4 (m/z = 230) was obtained through the SO<sub>2</sub> elimination of P5. Similar to pathway 1, P4 (m/z = 230) was also further attacked by 'OH to form product 2 (m/z = 124) and product 3 (m/z = 109) again. The oxidation products could be further degraded to small molecules, and finally mineralized to benign compounds, such as H<sub>2</sub>O, CO<sub>2</sub>.

Total organic carbon (TOC) was a typical mineralization index, and the PEC degradation of SMZ was assessed by the evolution of TOC. The degradation was carried out with 10 mg·L<sup>-1</sup> of SMZ, and the results was shown in Fig. S6. The TOC of SMZ solution decreased with the prolongation of illumination time. Over 40% of TOC was eliminated after 180 min, implying that SMZ could be partially mineralized by ZIF-8/ NF-TiO<sub>2</sub> under visible light irradiation.

#### 4. Conclusions

In the present study, a semiconductor-MOFs hybrid photo-electrocatalyst was successfully fabricated via in-situ growth method. Compared with unmodified TiO2-NTs, ZIF-8/NF-TiO2 heterogeneous photo-electrocatalyst exhibited many beneficial characteristics in charge generation and separation, such as the formation of anataserutile heterojunction, increased photocurrent response, improved the charge injection efficiency and reduced charge transfer resistance. Under the same conditions, the reaction rate and the degradation efficiency of ZIF-8/NF-TiO2 increased by 21.7 times and 11.6 times, respectively. Meanwhile, results in cyclic runs indicated excellent stability of the optimized photoanode. In the system, the degradation pathway of SMZ mainly be divided into three steps: cleaving, aromatic ring opening, and mineralizing. Superior PEC activity of ZIF-8/NF-TiO<sub>2</sub> was attributed to the following factors: (i) The doping of N and F could broaden absorption edge to the visible light region and promote the formation of N-Ti-O bonds, which suppressed the recombination of e<sup>-/</sup> h<sup>+</sup> pairs; (ii) The light penetrability and scattering properties of ZIF-8 led to higher light utilization; (iii) Double heterojunction structure among ZIF-8, rutile phase and anatase effectively promoted carriers transfer. As far as we know, this is the first report on photo-electrocatalysis of SMZ using semiconductor-MOFs as catalyst. Further efforts will focus on increasing the loading of MOFs, expanding the application of MOFs, and improving the PEC performance of film electrode. The new strategy reported here could enrich the design of novel semiconductor-MOFs hybrid photo-electrocatalysts.

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## Appendix A. Supplementary data

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