

Contents lists available at ScienceDirect

Applied Catalysis A, General



journal homepage: www.elsevier.com/locate/apcata

Photocatalytic H_2O_2 production using Ti_3C_2 MXene as a non-noble metal cocatalyst

Yiming Chen^a, Wenquan Gu^{a,b}, Li Tan^a, Zhimin Ao^{a,*}, Taicheng An^a, Shaobin Wang^{c,*}

^a Guangzhou Key Laboratory of Environmental Catalysis and Pollution Control, Guangdong Key Laboratory of Environmental Catalysis and Health Risk Control, School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou, 51006, China

^b Weng Yuan County Economic Development Zone, Shaoguan, 512600, China

^c School of Chemical Engineering and Advanced Materials, University of Adelaide, Adelaide, SA 5005, Australia

ARTICLE INFO

Keywords: TiO₂ Photocatalysis Ti₃C₂ MXene Cocatalyst H₂O₂ production

ABSTRACT

Photocatalytic H_2O_2 production by O_2 reduction is an environmental-friendly process for solar light conversion to chemical energy. In this work, Ti_3C_2 MXene was used as a non-noble metal cocatalyst to load on P25 as $Ti_3C_2/$ TiO_2 (TC/TO) photocatalysts for photocatalytic H_2O_2 synthesis. A H_2O_2 formation rate (179.7 µmol L⁻¹ h⁻¹) of the optimized 10 %-TC/TO composite was obtained to be over 21 folds as high as that of P25 under UV light. Radical quenching experiments and superoxide radical detection confirmed the superoxide radical as the primary intermediate, suggesting the O_2 reduction in two-step single-electron indirect reaction. The higher activity of TC/ TO can be attributed to the functions of Ti_3C_2 MXene in accelerating the separation and transfer of photogenerated electron-hole pairs, suppressing their recombination, and blocking the surface Ti—OOH formation. This work proves the promising roles of Ti_3C_2 MXene in the photocatalytic reaction and further expands their new applications in photocatalysis.

1. Introduction

Hydrogen peroxide (H_2O_2) has drawn much attention since it was first synthesized in 1818 [1]. It is well known that H_2O_2 is a clean and environmental-friendly multifunctional oxidant with water as a by-product only. H_2O_2 has been intensively used in environmental remediation and chemical industry, such as organic synthesis, pulp bleaching, disinfection, wastewater treatment and fuel cells [2–5]. Currently, the anthraquinone method, as the main method to synthesize H_2O_2 in industry, has some drawbacks, such as high costs, complicated synthesis routes and toxic by-products, which restrict its applications [1, 6]. Also, the direct synthesis route from O_2 and H_2 using noble metals (Pd or Au) or their alloy catalysts inevitably has a hazard of explosion [7–9]. Besides, electrocatalytic redox reaction synthesis of H_2O_2 also has the problem of high energy consumption [10]. Therefore, a facile, low energy consumption, eco-friendly, and safe alternative way to produce H_2O_2 is highly desirable.

Owing to the advantages of semiconductor photocatalysis, photocatalytic reaction is considered to be a promising approach to produce H_2O_2 with molecular oxygen (O_2) as the oxygen source and a sacrificial agent as the hydrogen source. A lot of semiconductor materials, TiO₂ [11–14], g-C₃N₄ [15–18], CdS [19,20], and BiVO₄ [21,22], have been explored in H₂O₂ generation via photocatalysis. Due to its stable structure, low cost and non-toxicity, TiO2 is the widely investigated photocatalyst so far [23]. Moreover, TiO₂ has a more negative conduction band potential (-0.19 V) than the reduction potential of O_2/H_2O_2 (0.695 V). Thus, in the presence of electron donors (ethanol, isopropanol or formic acid, etc), oxygen can be reduced to H₂O₂ by UV light. Nevertheless, the fast recombination of the photoinduced charge carriers and the Ti-OH groups on TiO2 surface severely hinder the formation of H₂O₂. Therefore, several techniques have been developed to design high-efficiency photocatalysts based on TiO₂, including surface complexation with ions [24,25], heterojunction construction [26], quantum-dots (QDs) modification [27,28], coupling with noble metal nanoparticle cocatalysts [11,29] and nonmetal doping [30], aiming at facilitating the separation of electron-hole pairs or restraining H₂O₂ decomposition, thereby improving the efficiency of photocatalytic H₂O₂ production. The applications of photocatalysis with non-noble metal cocatalysts were also studied using different metal oxides, metal chalcogenides, metal oxysulfide, metal phosphides, and even graphene to substitute scarce and expensive noble metal cocatalysts [31-35].

MXenes are two-dimensional materials as early transition metal

* Corresponding authors. *E-mail addresses:* zhimin.ao@gdut.edu.cn (Z. Ao), shaobin.wang@adelaide.edu.au (S. Wang).

https://doi.org/10.1016/j.apcata.2021.118127

Received 11 February 2021; Received in revised form 21 March 2021; Accepted 28 March 2021 Available online 2 April 2021 0926-860X/© 2021 Elsevier B.V. All rights reserved. nitrides, carbides, and carbonitrides in a typical molecular structure of M_{n+1}X_nT_x (M stands for an early d-block transition metal, X represents carbon and/or nitrogen, T_x is the surface termination functional group of -0, -OH and -F, and n = 1-3). Currently, they are typically prepared from the corresponding MAX phase precursors by selectively etching the A layers (usually Al element) with HF or LiF/HCl solution [36-38]. As a classic MXene, Ti₃C₂ has been widely applied in electrochemical energy storage [39], electromagnetic interference shielding [40], sensors [41] and cancer therapies [42] due to its excellent structural stability, high electrical conductivity, and hydrophilicity [43,44]. Apart from that, Ti₃C₂ MXene could be used as a noble-metal-free cocatalyst to couple with other semiconductor-based photocatalysts to form heterojunctions, which can be widely applied to carbon dioxide reduction reaction (CO₂RR), nitrogen reduction reaction (N₂RR), hydrogen evolution reaction (HER), oxygen evolution reaction (OER), pollutant degradation and other promising photocatalytic reactions [45,46]. For instance, Su et al. [47] reported an excellent performance of Ti₃C₂/g-C₃N₄ (2D/2D) nanosheets in photocatalytic hydrogen evolution. The hydrogen production reached 72.3 $\mu mol \; h^{-1} \; g_{cat}^{-1}, \, 10$ times higher compared to pristine g-C₃N₄. Wang et al. [48] found that Ti₃C₂ incorporated BiOCl presented a greatly improved removal of p-nitrophenol pollutant. The removal efficiency reached 98 % in 50 min and the degradation rate was nearly 3.3 times as high as that of pure BiOCl. Thus, Ti₃C₂ MXene was a superior synergistic catalyst to suppress effectively the recombination of the photogenerated electron-hole pairs and accelerate the electrons transfer process, enhancing the overall performance and increasing the reaction rate of catalysts. It is expected that the application of Ti₃C₂ MXene toward photocatalytic H₂O₂ production would be promising.

However, very few investigations have been reported using Ti_3C_2 MXene as a non-noble metal cocatalyst in photocatalytic H_2O_2 synthesis [49]. Herein, Ti_3C_2/TiO_2 photocatalysts were constructed by a simple impregnation method. Interestingly, Ti_3C_2 MXene can distinctly boost the performance of P25 for H_2O_2 generation under UV light irradiation. From the photoluminescence spectra, photocurrent analysis, electrochemical measurement, radical quenching tests and superoxide radical examination, we derived the possible mechanism of H_2O_2 production.

2. Experimental section

2.1. Chemicals and materials

Commercial P25 TiO₂ was obtained from Degussa. Titanium aluminum carbon (Ti₃AlC₂, 200 mesh) powder was bought from Jilin 11 Technology Co., Ltd. Disodium hydrogen phosphate (Na₂HPO₄) was provided by Tianjin DaMao Chemical Reagent Factory. Hydrofluoric acid (HF, 40 wt%) was received from Macklin. Absolute ethanol (C₂H₅OH), sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂, 30 wt%), and silver nitrate (AgNO₃) were obtained from Guangzhou Chemical Reagent Factory, while other materials and reagents including 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO), horseradish peroxidase (POD, RZ > 3.0), *N*,*N*-diethyl-p-phenylenediamine sulfate salt (DPD), sodium phosphate monobasic (NaH₂PO₄), sodium sulfate anhydrous (Na₂SO₄), p-benzoquinone (p-BQ), and methanol (CH₃OH), were purchased from Aladdin. All the reagents and chemicals were in a purity of analytical grade and ultrapure water was used in all experiments.

2.2. Synthesis of Ti₃C₂ MXene

According to the previous literature [50], 1 g Ti₃AlC₂ powders were slowly added to 60 mL HF solution in batches and the mixture was stirred at room temperature for 72 h. Then Ti₃C₂ was separated by a centrifuge and washed continuously several times using water and ethanol. The solid powders were collected and dried at 60 °C for 24 h in a vacuum oven. Finally, 30 mg of the obtained sample was dispersed and sonicated in 20 mL water for 1 h to obtain Ti₃C₂ solution at a concentration of 1.5 mg mL⁻¹.

2.3. Preparation of Ti_3C_2/TiO_2 composites

P25 TiO₂ (0.3 g) was added in 100 mL water under an ultrasound treatment for 30 min. Then, 4 mL Ti₃C₂ solution was added to the above P25 suspension drop by drop and stirred for another 30 min (the mass ratio of Ti₃C₂ MXene to P25 is 2 %). After stirring and standing for 30 min, a gray precipitate was collected and dried at 80 °C for 12 h in a vacuum oven, which was denoted as 2%-TC/TO. Similarly, other Ti₃C₂/TiO₂ composites with a different Ti₃C₂ loading (7 %, 10 %, 15 % and 20 %) were also prepared and were labeled as 7%-TC/TO, 10%-TC/TO, 15%-TC/TO, and 20%-TC/TO, accordingly.

2.4. Characterizations of catalysts

X-ray diffraction (XRD) patterns of P25 and its composites were performed by using an X-ray diffractometer with a Cu-Ka radiation source ($\lambda = 1.5218$ Å) (Bruker D8 ADVANCE). Transmission electron microscopy (TEM) images were collected on a Thermo Talos F200S field-emission transmission electron microscope operated at 200 kV. Field emission scanning electron microscopy (FE-SEM) with energydispersive X-ray spectroscopy (EDX) elemental mapping images were taken by a field-emission electron microscope (Hitachi SU8220) with an acceleration voltage of 15 kV. The specific surface area (Brunauer-Emmett-Teller, BET) of materials was measured on a Micromeritics ASAP2460 equipment using nitrogen adsorption-desorption isotherm. X-ray photoelectron spectroscopy (XPS) spectra were obtained from a Thermo Fisher Escalab 250Xi spectrometer with Al Ka radiation. Photoluminescence (PL) spectra were obtained using an Edinburgh FS5 fluorescence spectrophotometer under 380 nm excitation. UV-vis diffuse reflectance spectra (UV-vis DRS) were acquired on a Cary 300 spectrophotometer. The electron paramagnetic resonance (EPR) was conducted on a Bruker EMXplus-10/12 spectrometer under UV light irradiation.

2.5. Photocatalytic performance

Typically, a photocatalyst (50 mg) was uniformly dispersed in a mixture of 45 mL water and 5 mL ethanol in a quartz reactor. Before the irradiation, an adsorption experiment was conducted in dark for the adsorption-desorption equilibrium in 30 min and oxygen was continuously bubbled into the suspension. Then it was irradiated for 2 h under UV light ($\lambda = 365$ nm) which was provided by a 9 W white lamp (PCX50B) Discover, Beijing Perfectlight Technology Co., Ltd.). During the photocatalytic process, 1 mL of the solution was collected and filtered through a PES millipore filter (0.22 µm) to remove the photocatalyst powders at a given time interval. The quantity of generated H₂O₂ was analyzed by the DPD-POD method [51,52]. In this method, 1 mL of sample aliquots were mixed with 1.12 mL water, 0.4 mL phosphate buffered solution, 0.05 mL POD (1 mg mL⁻¹) and 0.05 mL DPD (10 mg mL⁻¹). After the mixture was kept stirring vigorously for a while, the absorbance of the mixed liquid was measured at 551 nm on a multifunctional microplate reader (Thermo Scientific, Varioskan LUX). The absorbance of H2O2 was measured three times. The photodecomposition of H₂O₂ was studied by adding 50 mg photocatalyst into 50 mL 0.4 mmol $L^{-1}\,H_2O_2$ solution for irradiation of 2 h under the similar condition as above.

2.6. Photocurrent and electrochemical measurements

The transient photocurrent analysis and electrochemical measurement were conducted on an electrochemical workstation (CHI 660E, Shanghai Chenhua, China) in a standard three-electrode system. The catalyst powder coated on a fluorine-doped tinoxide (FTO) glass substrate ($1 \times 1.5 \text{ cm}^2$) was applied as the working electrode. A Pt foil was used as the reference and a saturated Ag/AgCl electrode was employed as the counter electrode. The working electrode was synthesized as follows: 250 µL absolute ethanol and 12.5 µL Nafion solution (5 wt%)

were mixed with 5 mg catalyst by ultrasound-treated for 20 min. Then, 12.5 μ L catalyst suspension was uniformly dispersed on a FTO substrate and then dried at room temperature. The measurements were carried out in Na₂SO₄ electrolyte solution (0.2 M) under ambient condition. A 50 W lamp (PLS-FX300HU, Beijing Perfectlight Technology Co., Ltd.) was used in the photocurrent analysis.

3. Results and discussion

3.1. Characterizations of materials

The crystal structure and phase of the photocatalysts were studied by XRD patterns (Fig. 1a). After HF etching, the strongest diffraction peak (104) of Ti₃AlC₂ at about 39° disappeared. Due to the increase of the interlayer spacing, the (002) and (004) peaks of Ti₃C₂ MXene became broader and shifted to a lower angle compared to those of Ti₃AlC₂, indicating the removal of Al element from Ti₃AlC₂ to form Ti₃C₂ MXene [53]. Fig. 1b shows that all of the TC/TO materials present similar diffraction patterns to rutile TiO₂ (JCPDS: 21-1276) and anatase TiO₂ (JCPDS: 21-1272). Compared with the XRD pattern of P25, a very weak peak of Ti_3C_2 MXene appeared at about 9.8° after loading of Ti_3C_2 , which was caused by the low content of Ti_3C_2 in the TC /TO composites. With the increased loading of Ti_3C_2 , the characteristic peak of Ti_3C_2 becomes clearer in 20 %-TC/TO. In addition, no other new diffraction peaks can be detected, indicating no effect of Ti₃C₂ introduction on the crystal structure of P25 [54]. These results prove that Ti₃C₂ MXene was successfully compounded with P25.

The texture and morphology of Ti₃AlC₂, Ti₃C₂ MXene, P25 TiO₂ and 10 %-TC/TO were obtained through SEM measurements. As shown in Fig. 2a, bulky Ti₃AlC₂ exhibits a compact and layered ternary carbide structure. After HF etching treatment, the Al layers were disappeared and 2D accordion-like layered stacked structure of Ti₃C₂ MXene can be apparently found (Fig. 2b). Meanwhile, it can be observed that multiple monolayers are stacked in $\mathrm{Ti}_3\mathrm{C}_2$ MXene caused by ultrasonication and the thickness of the monolayer is about 5-20 nm. Fig. 2c presents the nanoparticles of P25 TiO2 with a uniform size, which are gathered together. Compared with Fig. 2b, the surface of Ti₃C₂ MXene flakes in Fig. 2d becomes rough and agglomerates with many nanoparticles. Interestingly, P25 nanocrystals are distributed evenly on the surface of Ti₃C₂ nanosheets and partially embedded in the lamella without severe aggregation, indicating that there is a strong bonding force between the P25 nanoparticles and Ti₃C₂ nanosheets. Ti₃C₂ MXene is wrapped by P25 nanoparticles in the composite material, thus ensuring that P25 can capture more light and facilitate the rapid transfer of charges from P25 to Ti₃C₂. From the HAADF-SEM and EDX elemental mapping images (Fig. 2e), it can be found that 10 %-TC/TO contains a large quantity of C,

Ti, O elements and relatively few F element from the surface-terminating functional groups of Ti_3C_2 MXene. The homogeneous dispersion of these elements in the 10 %-TC/TO photocatalyst indicates the successful preparation of the TC/TO nanocomposite.

The detailed morphology of 10 %-TC/TO was further observed from its TEM and high resolution TEM (HRTEM) images (Fig. 3). The size of P25 particles and the thickness of Ti_3C_2 flakes are at a nanoscaled level (Fig. 3a). From the HRTEM image in Fig. 3b, the obvious lattice fringes of P25 and Ti_3C_2 MXene can be clearly seen. The lattice spacing values of 0.27 and 0.35 nm are corresponding to the (0110) plane of Ti_3C_2 MXene and the (101) plane of anatase TiO_2 , respectively, indicating the successful synthesis of the 10 %-TC/TO composite and consistence with the SEM observations.

In general, the photocatalytic reaction mainly occurs on the photocatalyst surface and the surface area ultimately affects its photocatalytic performance. N₂ adsorption-desorption experiments (Fig. S1) presented the BET surface areas of the photocatalysts. The BET specific surface areas of P25 and 10 %-TC/TO are 48.5 and 56.0 m² g⁻¹, respectively, indicating that the introduction of Ti₃C₂ can improve the surface area of 10 %-TC/TO shows that the composite photocatalyst can provide more active sites for the reaction, which is expected to enhance the H₂O₂ production.

The surface chemical composition and state of the catalysts were measured from XPS. Fig. 4a shows the XPS survey spectra patterns of Ti₃C₂ MXene, 10 %-TC/TO and P25. The peak at around 75 eV corresponds to Al element in the survey spectra of Ti₃C₂, implying that a small amount of Al may remain in Ti₃C₂. The remaining Al may promote the adsorption of ethanol [55]. The peaks of Ti, C, O and F can be observed clearly in the spectra of 10 %-TC/TO, which was consistent with the EDX elemental mapping. F element related to the termination functional groups of Ti₃C₂ can be seen in 10 %-TC/TO, suggesting that the Ti₃C₂ was successfully incorporated into P25. Since the P25 occupies the main content in 10 %-TC/TO sample, the 10 %-TC/TO presented a similar XPS survey spectrum to that of P25. The C 1s XPS spectra of Ti₃C₂ MXene, 10 %-TC/TO and P25 are exhibited in Fig. 4b, while those of Ti 2p and O 1s in these samples are presented in Fig. 4c and d, respectively. For the C1s XPS spectra, the peak at 284.8 eV is referred to the adventitious elemental carbon [56]. Generally, the C 1s spectrum of Ti₃C₂ shows three other peaks at 288.8, 286.2 and, 281.6 eV, which are ascribed to the C-F, C-O, C-Ti bonds, respectively [57]. While 10 %-TC/TO exhibits two more characteristic peaks at 288.9 and 286.3 eV, which can be assigned to the C—O—Ti and C—O bonds, respectively. Then for Ti 2p XPS spectra, two typical peaks at 458.4 and 464.1 eV (Fig. 4c) are corresponding to the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ of the Ti—O bond in P25 [58], while they are presented at 458.6 and 464.3 eV in 10 %-TC/TO, which exhibit a positive shift of 0.2 eV in comparison with that in P25. Five



Fig. 1. XRD patterns of Ti₃C₂ MXene, Ti₃AlC₂ (a), and P25 as well as composites (b).



Fig. 2. SEM images of (a) Ti₃AlC₂, (b) Ti₃C₂ MXene, (c) P25 TiO₂ and (d) 10 %-TC/TO. (e) HAADF-SEM image and EDX elemental mapping of 10 %-TC/TO.



Fig. 3. TEM (a) and HRTEM images (b) of 10 %-TC/TO.

peaks at 454.8, 456.2, 459.1, 461.0 and 464.9 eV can be deconvoluted in the Ti 2p pattern of Ti₃C₂, which can be assigned to C—Ti (Ti 2p_{3/2}), O—Ti (Ti 2p_{3/2}), C—Ti (Ti 2p_{1/2}), O—Ti (Ti 2p_{1/2}) and F—Ti bonds, respectively [59,60]. After compounding with P25, the C—Ti (Ti 2p_{3/2}) and C—Ti (Ti 2p_{1/2}) of 10 %-TC/TO show the similar trend and their binding energies shift to higher positions (458.3 and 463.9 eV). Finally, for O 1s XPS spectra, Fig. 4d presents that the O 1s region of P25 is composed of two species (Ti—O—Ti and Ti—O—H) at 529.6 and 531.1 eV, respectively. However, they shift to 529.8 and 531.3 eV in 10 %-TC/TO, which also shows a positive shift of 0.2 eV (like Ti—O bonds). The changes of the bonding energy revealed that the electrons would be transferred from P25 to the Ti₃C₂ surface in 10 %-TC/TO, which was due to the strong interfacial interaction between the layered Ti₃C₂ and P25.

The UV-vis DRS spectra of various photocatalysts are described in Fig. 5. All of the photocatalysts based on P25 have an absorption edge

around 400 nm, attributing to the intrinsic light-harvesting capability of P25 [61]. Pure Ti₃C₂ does not show an absorption band due to its metallic nature [62]. Besides, it presents strong absorption in the entire wavelength range (200–800 nm), which is caused by its darker color. After the combination of Ti₃C₂ with P25, the light absorption intensity of the composite photocatalysts are higher than that of P25. Moreover, the increased loading of Ti₃C₂ in the composites leads to a color change from light to dark grey (Fig. S2) and the absorption intensity is greatly improved. The significantly enhanced light absorption of the TC/TO composite photocatalysts would facilitate the photocatalytic reaction of H₂O₂ production.

The PL technique is used to examine the separation efficiency of the photogenerated charge carriers on the semiconductor photocatalysts. Normally, the higher of the PL fluorescence intensity, the higher of the electron-hole recombination rate is [18,63]. From Fig. 6a, all of the PL



Fig. 4. (a) XPS survey spectra of Ti₃C₂ MXene, 10 %-TC/TO and P25, (b) High-resolution XPS C 1s spectra of Ti₃C₂ MXene and 10 %-TC/TO, (c) High-resolution XPS Ti 2p spectra of Ti₃C₂ MXene, 10 %-TC/TO and P25, and (d) High-resolution XPS O 1s spectra of 10 %-TC/TO and P25.



Fig. 5. UV-vis DRS spectra of P25, Ti₃C₂ MXene, and their composites.

spectra show a same emission peak at about 468 nm and 10 %-TC/TO displays a lower PL intensity than P25, demonstrating that the introduction of Ti₃C₂ can markedly decrease the recombination of the photogenerated electron-hole pairs and accelerate their separation. To further illustrate the spatial separation and transfer of the charge carriers in the photocatalytic process, some photoelectrochemical tests were performed [64,65]. The electrochemical impedance spectra (EIS) and transient photocurrent response curves were employed to evaluate the electronic conductivity and the charge carriers transfer ability on the semiconductor materials [66]. Fig. 6b suggests that all of the TC/TO composites have a higher photocurrent response compared with pristine P25 and 10 %-TC/TO sample exhibits the highest photocurrent among the composites, implying the better charge carriers transfer behavior of the 10 %-TC/TO sample. Generally, the smaller semicircle diameter of the Nyquist plots, the smaller the charge transfer resistance of the photocatalysts is. Fig. 6c illustrates clearly that 10 %-TC/TO composite material has the smallest semicircle radius among all the samples, suggesting that it owns the most efficient migration ability of the charge carriers. These results manifest that Ti₃C₂ MXene is an excellent cocatalyst to enhance the separation efficiency of the charge carriers and



Fig. 6. (a) PL spectra of P25, Ti₃C₂ MXene, and 10 %-TC/TO, (b) The transient photocurrent response curves of P25 and its Ti₃C₂ MXene composites, and (c) The electrochemical impedance spectra of P25, and its Ti₃C₂ MXene composites.

accelerate the migration of the spatial charge, thereby improving the photocatalytic activity.

3.2. Evaluation of photocatalytic H_2O_2 production

The photocatalytic performance of the TC/TO composites for H₂O₂ production was tested by O2 reduction in ethanol solution under UV light. The standard curve (Fig. S3) indicates a good linear relationship between the concentration of H_2O_2 and its absorbance ($R^2 = 0.991$). Ethanol was chosen as the final sacrificial agent because the yield of H₂O₂ was the highest in ethanol solution within 2 h (Fig. S4). Fig. 7a displays the time courses for H2O2 production of different photocatalysts. It can be clearly observed that bare Ti₃C₂ can hardly generate H₂O₂ and pure P25 also exhibits a poor activity toward H₂O₂ production due to its wide band gap, only 17.19 μ mol L⁻¹ of H₂O₂ detected after 2 h of UV light irradiation. Apparently, compounding Ti₃C₂ with P25 can dramatically improve the H₂O₂ generation. From Fig. 7b, 10 %-TC/TO photocatalyst possesses the best photocatalytic performance for H₂O₂ production among all the samples, and the concentration of H₂O₂ can reach a maximum of 359.43 μ mol L⁻¹ during the photocatalytic process, which is about 21 folds more than that of P25. Furthermore, the enhanced photocatalytic activity of 10 %-TC/TO exhibits higher H₂O₂ production than most of other TiO₂ based photocatalysts reported before (Table S1), indicating that the TC/TO composite is a promising photocatalyst for H₂O₂ generation. Besides, the recycling experiments were performed to determine the stability of 10 %-TC/TO for photocatalytic H₂O₂ production and the results are shown in Fig. S5. Unfortunately, due to the exposure of high proportion of metal atoms on the surface of Ti₃C₂ MXene, it is unstable in air (especially in oxygen), resulting in poor stability of 10 %-TC/TO. Further increasing loading of Ti₃C₂ made the yield of H₂O₂ gradually decrease. This phenomenon can be explained by the presence of excessive Ti₃C₂ in the composite materials, which can scatter light and lead to the light shielding effect.

Generally, formation and decomposition of H2O2 occur simultaneously during the photocatalytic reaction process. Therefore, we also investigated the photocatalytic H2O2 decomposition under various conditions, at an initial H_2O_2 concentration of 0.4 mmol L⁻¹ (Fig. 7c). H₂O₂ decomposes very slowly under UV light without any photocatalyst. In the presence of P25, H_2O_2 can be decomposed completely in 20 min. However, the decomposition rate of H2O2 under UV light was significantly decreased after Ti₃C₂ MXene loading. Owing to the few content of Ti₃C₂ in the 2 %-TC/TO samples, the decomposition of H₂O₂ is the same as that of pure P25. As the content of Ti₃C₂ increasing, the concentration of H₂O₂ decreased more slowly. The H₂O₂ decomposes at about 36.4 % on 10 %-TC/TO after UV irradiation of 2 h, far lower than that of P25. In the presence of P25, the decomposition rate of H₂O₂ is very fast, which is mainly due to the Ti-OH groups on the P25 surface. The Ti-OH groups can immediately react with H₂O₂ to form the peroxide complexes (Ti-OOH) by the light excitation and the Ti-OOH complexes can be decomposed to Ti-OH groups by electrons [67,68]. The coupling of Ti₃C₂ with P25 enables the photogenerated electrons generated from P25 to be rapidly transferred to Ti₃C₂. Thus, to some extent, the presence of Ti₃C₂ can inhibit the photodecomposition of H₂O₂, because the

introduction of Ti_3C_2 may reduce the formation of Ti—OOH complexes on the surface of the TC/TO photocatalysts.

3.3. The mechanism of enhanced photocatalytic performance

Generally, the photocatalytic production of H_2O_2 over TiO₂ photocatalysts can be achieved by a one-step two-electron direct reduction or a two-step sequential single-electron indirect reduction route. Apart from that, H_2O_2 can be generated through the reaction of the hydroxyl radicals formed by the oxidation of H_2O . To elucidate H_2O_2 generation pathway in the photocatalytic reaction, we conducted some control experiments. As exhibited in Fig. 8a, no production of H_2O_2 takes place in the absence of UV light irradiation, suggesting that the generation of H_2O_2 is accomplished by the photocatalysis. In addition, the amount of H_2O_2 generated is almost zero under N_2 atmosphere, indicating that this system cannot produce H_2O_2 in the absence of O_2 . Similarly, H_2O_2 can hardly be detected without ethanol, which shows the role of ethanol as a sacrificial agent. These results confirm that the formation of H_2O_2 is generally derived via the photoreduction of O_2 instead of holes induced H_2O oxidation [69].

In order to further prove whether H_2O_2 is produced through a sequential two-step single-electron O_2 reduction route or a direct twoelectron O_2 reduction, quenching experiments were carried out (Fig. 8b). The photocatalytic H_2O_2 generation was depressed and only 46.63 µmol L^{-1} of H_2O_2 can be detected in 2 h in the existence of 4 mM of AgNO₃, which usually acts as an efficient electron acceptor. However, the photocatalytic H_2O_2 generation was quenched completely with 4 mM p-BQ addition as a superoxide radical scavenger. A larger concentration of AgNO₃ (4 mol L^{-1}) was added and it was found that H_2O_2 could not be produced when electrons were completely quenched (Fig. S6). These results indicated that the photocatalytic generation of H_2O_2 in this system may be occurred via a sequential two-step single-electron indirect reduction route, where superoxide radical is an inevitable intermediate product of the photocatalytic reaction.

To confirm the presence of superoxide radical in the photocatalytic process, EPR tests were performed using DMPO as the spin trap. The EPR spectra were acquired with P25 and 10 %-TC/TO photocatalysts under UV light in methanol solution (Fig. 8c). It is noticeable that the typical EPR signal of DMPO- O_2^- with six peaks appeared after UV light illumination, suggesting the reduction of O_2 by the photo-generated electrons from P25 and 10 %-TC/TO photocatalysts. In addition, due to a good selectivity of nitroblue tetrazolium (NBT) toward O_2^- , it was chosen as a chemical probe to quantitatively analyze the production of O_2^- by detecting the decrease in its concentration at a wavelength of about 259 nm [30,70]. After the addition of 10 %-TC/TO, the concentration of NBT decreased more than that of P25 (Fig. S7), suggesting that the yield of O_2^- produced by 10 %-TC/TO photocatalyst is much more than that of P25, attributing to the enhanced separation and transfer of the photogenerated charges.

Based on the aforementioned results, we proposed a possible mechanism of photocatalytic H_2O_2 production over the Ti_3C_2/TiO_2 and schematically illustrated in Fig. 9. Photoexcitation of P25 TiO₂ can produce the pairs of electron (e⁻) and hole (h⁺) under UV light. The



Fig. 7. (a) Photocatalytic H₂O₂ production profiles, (b) Maximum yield of H₂O₂ production, and (c) Photodecomposition of H₂O₂ on various catalysts.



Fig. 8. (a) Photocatalytic H_2O_2 productions on 10 %-TC/TO under various conditions, (b) The quenching experiments of 10 %-TC/TO sample in H_2O_2 production, and (c) EPR spectra of DMPO- O_2^- adduct obtained with P25 and 10 %-TC/TO photocatalysts under UV light irradiation in methanol solution.



Fig. 9. The possible mechanism of photocatalytic $\rm H_2O_2$ production from $\rm Ti_3C_2/TiO_2$ photocatalyst.

electrons are transferred from the conduction band (CB) of TiO_2 to Ti_3C_2 MXene due to the dissimilar Fermi levels of the Ti_3C_2 and TiO_2 . The holes oxidize ethanol to provide the protons and the electrons react with O_2 to produce O_2^- and then H_2O_2 through a successive two-step singleelectron O_2 reduction reaction (Eqs. 1–3). The photocatalytic H_2O_2 production reaction can be described as follows.

$$CH_3CH_2OH + 2 h^+ \rightarrow CH_3CHO + 2H^+$$
(1)

$$O_2 + e^- \rightarrow O_2^- \tag{2}$$

$$O_2^- + 2H^+ + e^- \to H_2O_2$$
 (3)

On one hand, the loading of Ti_3C_2 on P25 can boost the separation of the photogenerated electrons from holes and their transfer. The increase of BET specific surface area will also provide more sites for H_2O_2 generation. On the other hand, the presence of Ti_3C_2 can prevent the Ti—OOH generation on the TC/TO surface to inhibit H_2O_2 decomposition. From a dynamic perspective, the formation rate of H_2O_2 increases and H_2O_2 decomposition rate decreases, leading to the increase in H_2O_2 concentration.

4. Conclusions

 Ti_3C_2 MXene was used as a 2D noble-metal-free cocatalyst for promoting photocatalytic H_2O_2 production in the Ti_3C_2/TiO_2 composites. Among the various photocatalysts, 10 %-TC/TO presented the best photocatalytic H_2O_2 generation. The maximum yield of H_2O_2 after 2 h of photocatalytic reaction can reach 359.43 µmol L⁻¹, about 21-fold higher than that of pristine P25. The addition of Ti_3C_2 can block the formation of surface Ti—OOH complexes and the intimate contact between P25 and Ti_3C_2 MXene promotes the separation and migration of the photogenerated electron-hole pairs. The EPR and radical quenching experiments demonstrated the evolution of $'O_2^-$ intermediate product during the photocatalytic H_2O_2 production, indicating that the predominant reaction pathway was the two-step single-electron indirect O_2 reduction.

Credit authorship contribution statement

Yiming Chen: Investigation, Data analysis, Writing - original draft. Wenquan Gu: Discussing - reviewing & editing. Li Tan: Data analysis. Zhimin Ao: Conceptualization, Supervision, Funding acquisition, Writing - review & editing. Taicheng An: Supervision. Shaobin Wang: Conceptualization, Supervision, Writing - reviewing & editing.

Declaration of Competing Interest

The authors report no declarations of interest.

Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (Grant No. 21777033), Science and Technology Program of Guangdong Province (2017B020216003), and Innovation Team Project of Guangdong Provincial Department of Education (2017KCXTD012).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.apcata.2021.118127.

References

- J.M. Campos-Martin, G. Blanco-Brieva, J.L.G. Fierro, Angew. Chem. Int. Ed. 45 (2006) 6962–6984, https://doi.org/10.1002/anie.200503779.
- [2] A. Asghar, A.A.A. Raman, W. Daud, J. Clean. Prod. 87 (2015) 826–838, https:// doi.org/10.1016/j.jclepro.2014.09.010.
- [3] L. Pi, J. Cai, L. Xiong, J. Cui, H. Hua, D. Tang, X. Mao, Chem. Eng. J. 389 (2020), 123420, https://doi.org/10.1016/j.cej.2019.123420.
- [4] C. Samanta, Appl. Catal. A Gen. 350 (2008) 133–149, https://doi.org/10.1016/j. apcata.2008.07.043.
- [5] S. Siahrostami, A. Verdaguer-Casadevall, M. Karamad, D. Deiana, P. Malacrida, B. Wickman, M. Escudero-Escribano, E.A. Paoli, R. Frydendal, T.W. Hansen, I. Chorkendorff, I.E.L. Stephens, J. Rossmeisl, Nat. Mater. 13 (2014) 97, https:// doi.org/10.1038/nmat3841.
- [6] G.-h. Moon, W. Kim, A.D. Bokare, N.-e. Sung, W. Choi, Synth. Lect. Energy Environ. Technol. Sci. Soc. 7 (2014) 4023–4028, https://doi.org/10.1039/c4ee02757d.
- [7] J.K. Edwards, B. Solsona, E.N. N, A.F. Carley, A.A. Herzing, C.J. Kiely, G. J. Hutchings, Science 323 (2009) 1037–1041, https://doi.org/10.1126/ science.1168980.
- [8] S. Kanungo, V. Paunovic, J.C. Schouteme, M.F.N. D'Angelo, Nano Lett. 17 (2017) 6481–6486. https://doi.org/10.1021/acs.nanolett.7b03589.
- [9] Y. Yi, L. Wang, G. Li, H. Guo, Catal. Sci. Technol. 6 (2016) 1593–1610, https://doi. org/10.1039/c5cv01567g.
- [10] E. Brillas, I. Sires, M.A. Oturan, Chem. Rev. 109 (2009) 6570–6631, https://doi. org/10.1021/cr900136g.
- [11] D. Tsukamoto, A. Shiro, Y. Shiraishi, Y. Sugano, S. Ichikawa, S. Tanaka, T. Hirai, ACS Catal. 2 (2012) 599–603, https://doi.org/10.1021/cs2006873.
- [12] X. Xiong, X. Zhang, S. Liu, J. Zhao, Y. Xu, Photochem. Photobiol. Sci. 17 (2018) 1018–1022, https://doi.org/10.1039/c8pp00177d.

- [13] X. Zeng, Z. Wang, N. Meng, D.T. McCarthy, A. Deletic, J.-h. Pan, X. Zhang, Appl. Catal. B Environ. 202 (2017) 33–41, https://doi.org/10.1016/j. apcatb.2016.09.014.
- [14] L. Zheng, J. Zhang, Y.H. Hu, M. Long, J. Phys. Chem. C. 123 (2019) 13693–13701, https://doi.org/10.1021/acs.jpcc.9b02311.
- [15] Y. Shiraishi, Y. Kofuji, H. Sakamoto, S. Tanaka, S. Ichikawa, T. Hirai, ACS Catal. 5 (2015) 3058–3066, https://doi.org/10.1021/acscatal.5b00408.
- [16] L. Tan, C. Nie, Z. Ao, H. Sun, T. An, S. Wang, J. Mater. Chem. A Mater. Energy Sustain. 9 (2020) 17–33, https://doi.org/10.1039/d0ta07437c.
- [17] Y.F. Wang, B.H. Jing, F.L. Wang, S.C. Wang, X. Liu, Z.M. Ao, C.H. Li, Water Res. 180 (2020), 115925, https://doi.org/10.1016/j.watres.2020.115925.
- [18] M. Wu, X. He, B.H. Jing, T. Wang, C.Y. Wang, Y.L. Qin, Z.M. Ao, S.B. Wang, T. C. An, J. Hazard. Mater. 384 (2020), 121323, https://doi.org/10.1016/j. jhazmat.2019.121323.
- [19] H.-I. Kim, O.S. Kwon, S. Kim, W. Choi, J.-H. Kim, Synth. Lect. Energy Environ. Technol. Sci. Soc. 9 (2016) 1063–1073, https://doi.org/10.1039/c5ee03115j.
- [20] S. Thakur, T. Kshetri, N.H. Kim, J.H. Lee, J. Catal. 345 (2017) 78–86, https://doi. org/10.1016/j.jcat.2016.10.028.
- [21] K. Fuku, Y. Miyase, Y. Miseki, T. Funaki, T. Gunji, K. Sayama, Chem.-Asian J. 12 (2017) 1111–1119, https://doi.org/10.1002/asia.201700292.
- [22] H. Hirakawa, S. Shiota, Y. Shiraishi, H. Sakamoto, S. Ichikawa, T. Hirai, ACS Catal. 6 (2016) 4976–4982, https://doi.org/10.1021/acscatal.6b01187.
- [23] L.N. Kong, X.T. Zhang, C.H. Wang, F.X. Wan, L. Li, Chin. J. Catal. 38 (2017) 2120–2131, https://doi.org/10.1016/s1872-2067(17)62959-0.
- [24] R.X. Cai, Y. Kubota, A. Fujishima, J. Catal. 219 (2003) 214–218, https://doi.org/ 10.1016/s0021-9517(03)00197-0.
- [25] V. Maurino, C. Minero, E. Pelizzetti, G. Mariella, A. Arbezzano, F. Rubertelli, Res. Chem. Intermed. 33 (2007) 319–332, https://doi.org/10.1163/ 156856707779238711
- [26] G.H. Moon, W. Kim, A.D. Bokare, N.E. Sung, W. Choi, Synth. Lect. Energy Environ. Technol. Sci. Soc. 7 (2014) 4023–4028, https://doi.org/10.1039/c4ee02757d.
- [27] T. Wang, C.Y. Nie, Z.M. Ao, S.B. Wang, T.C. An, J. Mater. Chem. A Mater. Energy Sustain. 8 (2020) 485–502, https://doi.org/10.1039/c9ta11368a.
- [28] L.H. Zheng, H.R. Su, J.Z. Zhang, L.S. Walekar, H.V. Molamahmood, B.X. Zhou, M. C. Long, Y.H. Hu, Appl. Catal. B Environ. 239 (2018) 475–484, https://doi.org/10.1016/j.apcatb.2018.08.031.
- [29] M. Teranishi, S.-i. Naya, H. Tada, J. Am. Chem. Soc. 132 (2010) 7850–7851, https://doi.org/10.1021/ja102651g.
- [30] X. He, M. Wu, Z. Ao, B. Lai, Y. Zhou, T. An, S. Wang, J. Hazard. Mater. 403 (2021) 124048, https://doi.org/10.1016/j.jhazmat.2020.124048.
- [31] D.Q. Zeng, W.J. Xu, W.J. Ong, J. Xu, H. Ren, Y.Z. Chen, H.F. Zheng, D.L. Peng, Appl. Catal. B Environ. 221 (2018) 47–55, https://doi.org/10.1016/j. apcatb.2017.08.041.
- [32] D.Q. Zeng, W.J. Ong, H.F. Zheng, M.D. Wu, Y.Z. Chen, D.L. Peng, M.Y. Han, J. Mater. Chem. A Mater. Energy Sustain. 5 (2017) 16171–16178, https://doi.org/ 10.1039/c7ta04816e.
- [33] D.Q. Zeng, P.Y. Wu, W.J. Ong, B.S. Tang, M.D. Wu, H.F. Zheng, Y.Z. Chen, D. L. Peng, Appl. Catal. B Environ. 233 (2018) 26–34, https://doi.org/10.1016/j. apcatb.2018.03.102.
- [34] Y.J. Yuan, Y. Yang, Z.J. Li, D.Q. Chen, S.T. Wu, G.L. Fang, W.F. Bai, M.Y. Ding, L. X. Yang, D.P. Cao, Z.T. Yu, Z.G. Zou, ACS Appl. Energ. Mater. 1 (2018) 1400–1407, https://doi.org/10.1021/acsaem.8b00030.
- [35] X. Lu, C.Y. Toe, F. Ji, W. Chen, X. Wen, R.J. Wong, J. Seidel, J. Scott, J.N. Hart, Y. H. Ng, ACS Appl. Mater. Interfaces 12 (2020) 8324–8332, https://doi.org/ 10.1021/acsami.9b21810.
- [36] M. Naguib, O. Mashtalir, J. Carle, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M. W. Barsoum, ACS Nano 6 (2012) 1322–1331, https://doi.org/10.1021/ nn204153h.
- [37] M. Naguib, J. Come, B. Dyatkin, V. Presser, P.-L. Taberna, P. Simon, M. W. Barsoum, Y. Gogotsi, Electrochem. commun. 16 (2012) 61–64, https://doi.org/ 10.1016/j.elecom.2012.01.002.
- [38] Y. Dall'Agnese, M.R. Lukatskaya, K.M. Cook, P.-L. Taberna, Y. Gogotsi, P. Simon, Electrochem. commun. 48 (2014) 118–122, https://doi.org/10.1016/j. elecom.2014.09.002.
- [39] M.R. Lukatskaya, O. Mashtalir, C.E. Ren, Y. Dall'Agnese, P. Rozier, P.L. Taberna, M. Naguib, P. Simon, M.W. Barsoum, Y. Gogotsi, Science 341 (2013) 1502–1505, https://doi.org/10.1126/science.1241488.
- [40] M.K. Han, X.W. Yin, H. Wu, Z.X. Hou, C.Q. Song, X.L. Li, L.T. Zhang, L.F. Cheng, ACS Appl. Mater. Interfaces 8 (2016) 21011–21019, https://doi.org/10.1021/ acsami.6b06455.

- [41] X. Chen, X.K. Sun, W. Xu, G.C. Pan, D.L. Zhou, J.Y. Zhu, H. Wang, X. Bai, B. A. Dong, H.W. Song, Nanoscale 10 (2018) 1111–1118, https://doi.org/10.1039/ c7nr06958h.
- [42] Z. Liu, M.L. Zhao, H. Lin, C. Dai, C.Y. Ren, S.J. Zhang, W.J. Peng, Y. Chen, J. Mater. Chem. B Mater. Biol. Med. 6 (2018) 3541–3548, https://doi.org/10.1039/ c8tb00754c.
- [43] M. Naguib, Y. Gogotsi, Accounts Chem. Res. 48 (2015) 128–135, https://doi.org/ 10.1021/ar500346b.
- [44] M. Naguib, V.N. Mochalin, M.W. Barsoum, Y. Gogotsi, Adv. Mater. 26 (2014) 992–1005, https://doi.org/10.1002/adma.201304138.
- [45] J. Chen, Q. Huang, H. Huang, L. Mao, M. Liu, X. Zhang, Y. Wei, Nanoscale 12 (2020) 3574–3592, https://doi.org/10.1039/c9nr08542d.
- [46] J. Zhou, G. Liu, Q. Jiang, W. Zhao, Z. Ao, T. An, Chin. J. Catal. 41 (2020) 1633–1644, https://doi.org/10.1016/s1872-2067(20)63571-9.
- [47] T.M. Su, Z.D. Hood, M. Naguib, L. Bai, S. Luo, C.M. Rouleau, I.N. Ivanov, H.B. Ji, Z. Z. Qin, Z.L. Wu, Nanoscale 11 (2019) 8138–8149, https://doi.org/10.1039/ c9nr00168a.
- [48] C.J. Wang, J. Shen, R.G. Chen, F. Cao, B. Jin, Appl. Surf. Sci. 519 (2020), 146175, https://doi.org/10.1016/j.apsusc.2020.146175.
- Y. Yang, Z. Zeng, G. Zeng, D. Huang, R. Xiao, C. Zhang, C. Zhou, W. Xiong,
 W. Wang, M. Cheng, W. Xue, H. Guo, X. Tang, D. He, Appl. Catal. B Environ. 258 (2019), 117956, https://doi.org/10.1016/j.apcatb.2019.117956.
- [50] M. Lu, W. Han, H. Li, W. Shi, J. Wang, B. Zhang, Y. Zhou, H. Li, W. Zhang, W. Zheng, Energ. Storage Mater. 16 (2019) 163–168, https://doi.org/10.1016/j. ensm.2018.04.029.
- [51] C. Wang, M.C. Long, B.H. Tan, L.H. Zheng, J. Cai, J.J. Fu, Electrochim. Acta 250 (2017) 108–116, https://doi.org/10.1016/j.electacta.2017.08.052.
- [52] B. Weng, J. Wu, N. Zhang, Y.J. Xu, Langmuir 30 (2014) 5574–5584, https://doi. org/10.1021/la4048566.
- [53] Y. Sun, D. Jin, Y. Sun, X. Meng, Y. Gao, Y. Dall'Agnese, G. Chen, X.-F. Wang, J. Mater. Chem. A Mater. Energy Sustain. 6 (2018) 9124–9131, https://doi.org/ 10.1039/c8ta02706d.
- [54] V. Repousi, A. Petala, Z. Frontistis, M. Antonopoulou, I. Konstantinou, D. I. Kondarides, D. Mantzavinos, Catal. Today 284 (2017) 59–66, https://doi.org/ 10.1016/j.cattod.2016.10.021.
- [55] T. Hou, Q. Luo, Q. Li, H. Zu, P. Cui, S. Chen, Y. Lin, J. Chen, X. Zheng, W. Zhu, S. Liang, J. Yang, L. Wang, Nat. Commun. 11 (2020) 4251, https://doi.org/ 10.1038/s41467-020-18091-7.
- [56] C. Zhou, C. Lai, D. Huang, G. Zeng, C. Zhang, M. Cheng, L. Hu, J. Wan, W. Xiong, M. Wen, X. Wen, L. Qin, Appl. Catal. B Environ. 220 (2018) 202–210, https://doi. org/10.1016/j.apcatb.2017.08.055.
- [57] S. Cao, B. Shen, T. Tong, J. Fu, J. Yu, Adv. Funct. Mater. 28 (2018), 1800136, https://doi.org/10.1002/adfm.201800136.
- [58] W. Yuan, L. Cheng, Y. Zhang, H. Wu, S. Lv, L. Chai, X. Guo, L. Zheng, Adv. Mater. Interfaces 4 (2017), 1700577, https://doi.org/10.1002/admi.201700577.
- [59] J.X. Low, L.Y. Zhang, T. Tong, B.J. Shen, J.G. Yu, J. Catal. 361 (2018) 255–266, https://doi.org/10.1016/j.jcat.2018.03.009.
- [60] Z.W. Zhang, H.N. Li, G.D. Zou, C. Fernandez, B.Z. Liu, Q.R. Zhang, J. Hu, Q. M. Peng, ACS Sustain. Chem. Eng. 4 (2016) 6763–6771, https://doi.org/10.1021/ acssuschemeng.6b01698.
- [61] K. Cheng, W. Sun, H.-Y. Jiang, J. Liu, J. Lin, J. Phys. Chem. C. 117 (2013) 14600–14607, https://doi.org/10.1021/jp403489r.
- [62] J. Ran, G. Gao, F.-T. Li, T.-Y. Ma, A. Du, S.-Z. Qiao, Nat. Commun. 8 (2017), 13907, https://doi.org/10.1038/ncomms13907.
- [63] T. Su, H. Tian, Z. Qin, H. Ji, Appl. Catal. B Environ. 202 (2017) 364–373, https:// doi.org/10.1016/j.apcatb.2016.09.035.
- [64] H.L. Tan, F.F. Abdi, Y.H. Ng, Chem. Soc. Rev. 48 (2019) 1255–1271, https://doi. org/10.1039/c8cs00882e.
- [65] H. Wu, H.L. Tan, C.Y. Toe, J. Scott, L. Wang, R. Amal, Y.H. Ng, Adv. Mater. 32 (2020), 1904717, https://doi.org/10.1002/adma.201904717.
- [66] Y. Yang, Z.T. Zeng, C. Zhang, D.L. Huang, G.M. Zeng, R. Xiao, C. Lai, C.Y. Zhou, H. Guo, W.J. Xue, M. Cheng, W.J. Wang, J.J. Wang, Chem. Eng. J. 349 (2018) 808–821, https://doi.org/10.1016/j.cej.2018.05.093.
- [67] H. Hou, X. Zeng, X. Zhang, Angew. Chem. Int. Ed. 59 (2020) 17356–17376, https://doi.org/10.1002/anie.201911609.
- [68] H. Sheng, H.W. Ji, W.H. Ma, C.C. Chen, J.C. Zhao, Angew. Chem. Int. Ed. 52 (2013) 9686–9690, https://doi.org/10.1002/anie.201304481.
- [69] Y. Zheng, Z.H. Yu, H.H. Ou, A.M. Asiri, Y.L. Chen, X.C. Wang, Adv. Funct. Mater. 28 (2018), 1705407, https://doi.org/10.1002/adfm.201705407.
- [70] D. Xia, Z. Shen, G. Huang, W. Wang, J.C. Yu, P.K. Wong, Environ. Sci. Technol. 49 (2015) 6264–6273, https://doi.org/10.1021/acs.est.5b00531.