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Research Article

Keywords: photoelectrocatalytic, formaldehyde, TiO2, Fe2O3, DFT

DOI: https://doi.org/10.21203/rs.3.rs-164964/v1

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Improvement of Water Resistance by Fe$_2$O$_3$/TiO$_2$

Photoelectrocatalysts for Formaldehyde Removal:
Experimental and Theoretical Investigation

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TiO₂-based photocatalysts are a potential technology for removing indoor formaldehyde (CHOH) owing to their strong photooxidation ability. However, their photooxidation performance is generally weakened when suffering from the competitive adsorption of H₂O. In a method inspired by the oxygen evolution reaction (OER) to generate intermediates with hydroxyl radicals on the anode electrode catalysts, an electric field was employed in this research and applied to the photooxidation of CHOH to prevent the competitive adsorption of H₂O. Additionally, 0.5-5% Fe₂O₃ decorated TiO₂ was employed to improve the photoelectrocatalytic activity. The influence of an electric field on hydroxyl-radical production was investigated by both density functional theory (DFT) with direct-imposed dipole momentum and photoelectrocatalytic experimental tests. The surface characterization of the photocatalysts, including transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and electron paramagnetic resonance (EPR), was conducted. DFT results show that a positive electric field with a strength of 0.05 Å/V was more favorable to produce hydroxyl on Fe₂O₃/TiO₂(010) than was a negative electric field. Fe₂O₃ decoration can significantly boost hydroxyl formation, resulting from a decrease in the binding energy between the Fe of Fe₂O₃ and the oxygen and hydrogen atoms of H₂O. The dissociated hydrogen atom of the H₂O preferentially remained on the catalysts’ surface rather than being released into the gas flow. The experimental results demonstrated that the application of a low-voltage of 150 V could not directly enhance the photooxidation of CHOH by either TiO₂ or Fe₂O₃/TiO₂ but that
it could relieve the H$_2$O inhibitory effect by more than 10% on the Fe$_2$O$_3$/TiO$_2$.

**Keywords:** photoelectrocatalytic; formaldehyde; TiO$_2$; Fe$_2$O$_3$; DFT
1. Introduction

Formaldehyde (CHOH) is one of China’s most harmful indoor air pollutants and poses a dangerous threat to human health (Kim et al., 2011; Tang et al., 2009). Various removal technologies including adsorption (Yang et al., 2017), solvent absorption (Yang et al., 2017), catalytic conversion (Guo et al., 2019; Li et al., 2020; Miao et al., 2019; Nie et al., 2016), and photooxidation, can effectively address indoor CHOH pollution. Due to their photoinduced holes and electrons, photocatalysts can produce highly oxidative hydroxyl or superoxide radicals, thus being good candidates for the photooxidation of CHOH (Wang et al., 2017; Yu et al., 2013; Zhang et al., 2017). However, because of the competitive adsorption of the oxygen in H₂O and the carbonyl group in CHOH, photocatalysts suffer from H₂O interference with several-order concentrations higher than CHOH under a specific humidity, which would enormously undermine their photocatalytic activity. A key to solving the inhibitory effect of gaseous H₂O is activating the H₂O molecule and producing more surface hydroxyl radicals. However, H₂O splitting for hydroxyl production cannot proceed spontaneously and requires an enormous amount of energy to overcome the energy barrier of hydroxyl formation (Chen et al., 2014; Ding et al., 2018). It is well known that under overpotentials in an electrochemical cell, the oxygen evolution reaction (OER) on anode catalysts produces an intermediate of hydroxyl radicals by abstracting one hydrogen atom of H₂O. Then, the released electrons are transported to the anodes, following Eq. (1) below,

\[ \text{H}_2\text{O} + * \rightarrow \text{*OH} + \text{H}^+ + \text{e}^- \] (1)
where * represents the coordinatively unsaturated sites of the catalyst (Valdés et al., 2008). Although the OER commonly occurs in an aqueous environment, it is vital to experimentally and theoretically investigate whether it can proceed between a gas-solid interface. Another question was whether photooxidation of gaseous H₂O to produce hydroxyls could be strengthened under an external electric field, thus substantially enhancing the removal of CHOH.

Theoretical calculation methods are currently employed to simulate the electrochemical catalysis, including

(a) The computational hydrogen electrode (CHE) method, proposed by Nørskov et al. (Nørskov et al., 2004);

(b) A double reference method with a modification of the electrical double layer (EDL) (Filhol and Neurock, 2006; Lozovoi and Alavi, 2003);

(c) Direct-imposed dipole momentum on a periodic surface slab representing an electric field (Deshlahra et al., 2009; Jörg and Matthias, 1992).

The CHE model can successfully analyze the overpotential of the OER on a none charged catalyst slab, but it is difficult to simulate the dependence of physiochemical adsorption on an applied external field. The EDL model could well reflect the dependence by adding one or more extra charges and identical compensating charges, which is suitable for analyzing a liquid-solid slab system (Duan and Henkelman, 2019; Filhol and Neurock, 2006). The third method is widely used to simulate a charged gas-solid catalytic reaction system by introducing a dipole momentum on a slab + adsorbates to embody an external electrostatic field (Deshlahra et al., 2009; Jörg and
Herein, the third method of introducing a dipole moment as implemented in Vienna Ab-initio Simulation Package (VASP) was employed to investigate the synergetic effect of photoelectrocatalytic oxidation on the formation of \(-\text{OH}\). It is worth noting that unlike when a hydrogen atom diffuses into the electrolyte after producing a hydroxyl radical (\(\cdot\text{OH}\)) on a liquid-solid interface, hydrogen would be attached to catalysts or transported away by carrier gases on a gas-solid interface. Accordingly, the free energy of the formation of the two terminates was calculated in this research, where (a) one remains on the catalyst’s surface as \(-\text{OH} + \text{H}^+\) and (b) the other leaves to form \(-\text{OH}+\text{H}^+\text{(gas)}\).

\(\text{TiO}_2\), due to its strong photoredox ability, excellent chemical stability, low cost, and few secondary derivatives, has been widely investigated for photodegrading formaldehyde. Under UV irradiation, strong oxidative free radicals, \(\cdot\text{O}_2^-\) and \(\cdot\text{OH}\), are produced at the surface of \(\text{TiO}_2\) and can effectively react with \(\text{CHOH}\) to form formate and the final products of \(\text{CO}_2\) and \(\text{H}_2\text{O}\) (Sun et al., 2010; Tasbihi et al., 2015). Thus, it has great potential to be employed as a commercial photocatalyst inside air cleaners to treat indoor \(\text{CHOH}\) (Cremer et al., 2014; Liang et al., 2012). However, because of the rapid recombination of photoinduced electron-hole pairs for \(\text{TiO}_2\), the photocatalytic activity of \(\text{TiO}_2\) is not high enough to degrade \(\text{CHOH}\) efficiently (Yu et al., 2013). How to slow the recombination of photogenerated electron-hole pairs plays a vital role in enhancing the photocatalytic activity of \(\text{TiO}_2\).

Thus, a material with low resistance or impedance to modify \(\text{TiO}_2\) is needed to enhance photodegrading \(\text{CHOH}\) assisted with an electric field. \(\text{Fe}_2\text{O}_3\), a cheap
ferromagnetic material, possesses good electrical properties, such as high capacity, high charging rate, long-life usage, and low resistance, which can effectively decrease the insulating behavior of TiO$_2$ (Piva et al., 2016; Ding et al., 2017). Additionally, the interface of Fe$_2$O$_3$ and TiO$_2$ can accelerate the transfer of photoinduced electrons from the conduction band of Fe$_2$O$_3$ to that of TiO$_2$ (Moniz et al., 2014; Wang et al., 2014). Thus, decorating Fe$_2$O$_3$ on TiO$_2$ was employed to enhance the photoelectrical activity.

Therefore, the photoelectrical catalytic oxidation of H$_2$O to produce hydroxyl on TiO$_2$ and Fe$_2$O$_3$ decorated TiO$_2$ was explored using DFT calculations. The surface characterization of photocatalysts, including transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), was conducted. Furthermore, this study experimentally investigated the photoelectrical catalytic oxidation of gaseous CHOH by Fe$_2$O$_3$-decorated TiO$_2$ under an external electric field with and without humidity.

**Experimental Methods**

2.1 Preparation for Fe$_2$O$_3$/TiO$_2$

Fe$_2$O$_3$/TiO$_2$ was prepared by the impregnation method. A weight of 1.00 g commercial TiO$_2$ (Tianhe Environmental Engineering Co., Ltd., Baoding) was mixed into 70 mL distilled water and then stirred continuously for 30 min at room temperature. Then, 0.5%, 3.0%, and 5% Fe$_2$O$_3$/TiO$_2$ samples were prepared by adding 0.025, 0.150, and 0.250 g FeCl$_3$·6H$_2$O into the TiO$_2$ solution, respectively. After continuous stirring for 90 min at room temperature, the mixtures were dried at 105°C in a rotary evaporator at a reduced pressure of 0.01 kPa to dry the residue H$_2$O. Then, the dried samples were
calcinated at 500 °C for 12 h in an air atmosphere to form Fe$_2$O$_3$/TiO$_2$. Before each

CHOH degrading test, the prepared Fe$_2$O$_3$/TiO$_2$s catalysts were loaded onto glass fiber

as follows: 1.0 g photocatalysts were dispersed in 1 L of distilled water with ultrasonic
treatment for 10 min. Cylindrical glass fiber was immersed in the Fe$_2$O$_3$/TiO$_2$ solution
for at least 5 h and then dried for 2 h at 105 °C. The filled amount of Fe$_2$O$_3$/TiO$_2$ was
the weight difference of the glass fiber before and after the loading treatment.

2.2 Characterization of Fe$_2$O$_3$/TiO$_2$

A scanning electron microscope (SEM) was used to obtain the morphologies of
the Fe$_2$O$_3$/TiO$_2$s with a beam accelerating voltage and current of 20 kV and 20 μA,
respectively. High-resolution transmission electron microscopy (HR-TEM) was
performed on a Tecnai G2 F20 (FEI, USA) with an accelerating voltage of 200 kV. An
X-ray diffraction (XRD) analyzer was used to analyze the crystal pattern of TiO$_2$ and
Fe$_2$O$_3$/TiO$_2$(s) with a Shimadzu X-ray beam with Cu-Ka radiation. Raman spectra of
the specimens were obtained using a SenterraII (BRUCK, USA) with a scanning range
of 100-1000 cm$^{-1}$. The photoluminescence spectra (PL) of the TiO$_2$ and Fe$_2$O$_3$/TiO$_2$s
catalysts were recorded on a Varian Cary Eclipse spectrometer with an excitation
wavelength of 325 nm. UV-vis spectra of the photocatalysts were recorded in the range
of 200-800 nm by a Shimadzu UV-vis (UV-2550) spectrometer equipped with a diffuse
reflection accessory. BaSO$_4$ was employed as the reference substance. Electrochemical
impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) were performed
using an electrochemical workstation (CHI604E, C.H. Inc.). The EIS and LSV were
measured at a constant A.C. amplitude of 5.0 mV with a sweep frequency of 10$^5$-0.1
Hz. The voltage ranged from -0.3 to 0.2 V for the LSV measurement with 0.1 M Na\textsubscript{2}SO\textsubscript{4} solution as the electrolyte. The Mott-Schottky plots were established with the A.C. amplitude of 10 mV at 100 Hz. The sweep voltage ranged from -1.2 to 0.5 V. The EPR measurements were performed using a Bruker ER200D operated in the X-band. Approximately 10-50 mg of photocatalyst was placed into a particular spectroscopically pure quartz cell.

2.3 DFT experimental methods

The commercial TiO\textsubscript{2} exhibits a predominantly exposed (010) facet, which was also illustrated in the following TEM characterization results. Thus, an anatase TiO\textsubscript{2} (010) slab was constructed to simulate the TiO\textsubscript{2} base. Before constructing the slab, we first optimized the unit cell of anatase TiO\textsubscript{2}. The crystal lattice spacing was optimized to be $a = b = 3.80$ and $c = 9.50$ Å; this optimization was in agreement with previous research (Shen et al., 2021). The TiO\textsubscript{2}(010) slab consisted of four layers and 48 atoms ($\text{Ti}_{16}\text{O}_{32}$), and a vacuum height of 20 Å oriented along the c-axis. The Fe\textsubscript{2}O\textsubscript{3} decoration was assembled by loading one (Fe\textsubscript{2}O\textsubscript{3}) cluster consisting of 2 Fe and 3 O atoms on the TiO\textsubscript{2}(010), as shown in Figure 9. An external electric field was applied vertically to the slab by an approach proposed by Naugebeaur and Scheffler. Positive and negative electric fields with strengths of 0.05 and -0.05 eV/Å were imposed on the supercell to simulate different electric-field directions. A positive external electric field led to a distribution of positive charges on the upper side of the slab, and the negative external electric field led to opposite results (Deshlahra et al., 2009). The formation of hydroxyl radicals with (or without) the dissociated hydrogen atom of H\textsubscript{2}O connected on TiO\textsubscript{2}(010)
and \( \text{Fe}_2\text{O}_3/\text{TiO}_2(010) \) was constructed as follows: for the case of hydrogen atoms anchored at the surface, the hydroxyl was connected to an unsaturated five-coordinate Ti atom (Ti\(_{5c}\)) and an atop four-coordinate Fe atom (Fe\(_{4c}\)), for \( \text{TiO}_2(010) \) and \( \text{Fe}_2\text{O}_3/\text{TiO}_2(010) \), respectively. The hydrogen atom was then linked to the adjacent oxygen atom of the Ti\(_{5c}\) (Fe\(_{4c}\)) on \( \text{TiO}_2(010) \) (Fe\(_2\text{O}_3/\text{TiO}_2(010) \)). In the absence of hydrogen, which was taken away from slabs, only a hydroxyl was bonded to the Ti\(_{5c}\) (Fe\(_{4c}\)) for the \( \text{TiO}_2(010) \) (Fe\(_2\text{O}_3/\text{TiO}_2(010) \)). The free energies of hydroxyl formation with \( \Delta G^*-\text{OH} + ^*\text{H} \) and without hydrogen \( \Delta G^*-\text{OH} \) under an external electric field were determined by Eqs. (2)-(3), respectively,

\[
\Delta G^*-\text{OH} + ^*\text{H} = G^*-\text{OH} + ^*\text{H} - G_{\text{bare}^*} - G_{\text{H}_2\text{O}(g)} - eU \quad (2)
\]

\[
\Delta G^*-\text{OH} = G^*-\text{OH} - G_{\text{bare}^*} - G_{\text{H}_2\text{O}(g)} + 1/2G_{\text{H}_+} - eU \quad (3)
\]

where \( G^*-\text{OH} + ^*\text{H} \) and \( G^*-\text{OH} \) are the free energies of hydroxyl (with or without hydrogen atoms) connected to charged \( \text{TiO}_2(010) \) and \( \text{Fe}_2\text{O}_3/\text{TiO}_2(010) \) and calculated within the applied electric field. \( G_{\text{bare}^*} \) is the free energy of the charged catalysts within the electric field without any hydroxyl or hydrogen atom from \( \text{H}_2\text{O} \). \( G_{\text{H}_2\text{O}(g)} \), and \( G_{\text{H}_+} \) are the free energies of \( \text{H}_2\text{O} \) and hydrogen atoms without any charges, respectively, which were calculated in the absence of an external electric field. \( U \) is the overpotential relative to the standard potential of a hydrogen electrode. Additionally, the difference in zero-point energies and the entropy change in \( T\Delta S \) were corrected by determining the vibrational frequencies of the adsorbed \( -\text{OH} \) with and without hydrogen (Valdés et al., 2008). The reaction temperature was set to 298 K.

The correction for \( \Delta G^*-\text{OH} + ^*\text{H} \) or \( \Delta G^*-\text{OH} \) at a neutral pH and in an ambient
environment was also carried out based on Nernst’s equation by Eq. (4). Herein, the
photocatalysts were enveloped under neutral conditions without any acid or alkaline
components in the continuous injection of gaseous H$_2$O. Thus, the pH was set to 7.0 to
simulate the neutral environment on the gas-solid interface.

$$\Delta G_{pH}(pH) = 2.30 \times k_B T \times pH$$  \hspace{1cm} (4)

The model calculation was determined based on the generalized gradient
approximation with the Perdew-Burke-Ernzerhof exchange-correlation function
(GGA-PBE). Hubbard U values ($U_{\text{eff}}$) of 4.20 and 5.00 eV were applied for Ti 3d and
Fe 3d atomic orbitals, respectively, referring to previous research (Shim et al., 2009).
The Brillouin zone was determined automatically with the gamma center in the
Monkhorst-Pack scheme. The energy cutoff was set to 400 eV. The convergence criteria
for the energy (EDIFF) and force (EDIFFG) were $10^{-4}$ eV and -0.02 eV/Å, respectively.
All atoms in the slabs were relaxed in all the structure optimizations. All the
determinations mentioned above were performed with the VASP.

2.4 Photoelectrocatalytic measurements

The photoelectrocatalytic reaction system consisted of a CHOH generation
system, a photoelectric catalytic reactor, and an online detector, as shown in Figure 1.
Gaseous CHOH was produced from a permeable tube enclosed in a U-shaped glass tube
filled with a few glass beads to keep the influent gas cross-sectionally uniform. The U-
shaped tube was placed in a water bath at a constant temperature of 80°C. Pure N$_2$
(99.99%) was used as the carrier gas. The influent concentration of CHOH was set to
1.50 ppm for each test. Additionally, O$_2$ (99.9%) and H$_2$O($g$) were also injected into the
reactor. Different humidities of the influent gas flow were adjusted by changing the
flow rate of N\textsubscript{2} purged into an impinger bottle containing water, which was measured
by a humidity detector. The overall influent flow rate was set to 700 mL/min. Before
entering the reactor, all the gas components were thoroughly mixed in a chamber, which
contained a magnetic stirrer, at a stirring rate of 200 r/min. All pipelines were made of
polytetrafluoroethylene to prevent the adhesion of the CHOH. The
photoelectrochemical reactor had a cylindrical shape with a height of 600 mm and an
interior diameter of 150 mm. A quartz cover on the top of the reactor was used to receive
UV irradiation. A UV lamp (\(\lambda=254\) nm, \(P = 15\) W) was placed directly above the reactor
at a distance of 15 cm from the fixed catalysts, and the fluence rate (\(\psi\)) was evaluated
to be 5.3 mW/cm\textsuperscript{2}. Two pieces of round woven mesh made of stainless steel were used
not only as a support for catalyst-coated glass fibers but also as the positive and negative
electrodes, which were connected with a self-designed direct-current (DC) voltage
output device. To avoid the consumption of energy, the supplied power (P) was as low
as 5 W. The output voltage between the two electrodes was measured to be
approximately 150 V. Correspondingly, the strength of the electric field was determined
to be 5000 V/m since the distance between the two pieces of woven mesh was
approximately 3.0 cm. For each test, the fiberglass filter coated with Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} was
sandwiched between the woven mesh. The superficial velocity for the photoelectric
reaction was determined to be 3.96 cm/min. The reaction temperature inside the reactor
was approximately 25\textdegree C. A working air conditioner was used to cool the reactor. A
CHOH detector (4160-19.99 m, Interscan) was used to monitor the effluent
concentration of CHOH online.

The removal efficiency was determined as the ratio of the difference in the influent and effluent concentrations of CHOH over the influent concentration, as shown in Eq. (5) described,

\[ \eta = \frac{C_0 - C_i}{C_0} \times 100\% \]  

where \( C_0 \) (ppm) is the influent concentration of CHOH, and \( C_i \) (ppm) is the effluent concentration of CHOH.

The removal rate \( r \) was calculated as the mass of CHOH reduced per unit time (min) and unit mass catalyst (g) described below:

\[ r = (C_0 - C_i) \times \frac{M_{\text{CHOH}} \times Q}{24,450 \times m} \text{ (ng/min/g)} \]  

where \( M_{\text{CHOH}} \) is the molar mass of CHOH (30 g/mol), \( Q \) is the overall influent flow rate (700 mL/min), and \( m \) is the catalyst mass (g) loading on the glass fibers.

3 Results and discussion

3.1 Surface characterization of TiO\(_2\) and Fe\(_2\)O\(_3\)/TiO\(_2\)

3.1.1 Morphology of TiO\(_2\) and Fe\(_2\)O\(_3\)/TiO\(_2\)

Figure 2 shows the SEM and TEM morphologies of the commercial TiO\(_2\) and 5\%Fe\(_2\)O\(_3\)/TiO\(_2\). The morphologies of TiO\(_2\) and Fe\(_2\)O\(_3\)/TiO\(_2\) exhibited similar granule shapes according to SEM (Figure 2(a) and (e)). The TEM images of TiO\(_2\) clearly showed that most of these granules displayed elongated tetragonal cuboids with a d-space of 0.37 nm in Figure 2(b), which highly approached that of the exposed facet of the (010) plane (Pan et al., 2011). Thus, we inferred that the (010) plane accounted for a considerably large proportion of the exposed facet of the TiO\(_2\). Additionally, a minor
portion of granules with a d-space of 0.24 nm was attributed to the (103) plane (Ciancio et al., 2012). The average diameter of the TiO$_2$ granules was statistically estimated to be 12.9±4.9 nm, as shown in Figure 2(d). After the decoration of Fe$_2$O$_3$, the 3.0% Fe$_2$O$_3$/TiO$_2$ also presented a primarily cuboid shape similar to that of TiO$_2$ (Figures 2(f)-(g)). The primary d-space of the 3.0% Fe$_2$O$_3$/TiO$_2$ cuboid granule was measured to be 0.37 nm, corresponding to the (010) plane, and 0.25 nm for the minor interplane space, assigned to the (110) anatase plane. Thus, the morphology of the prepared Fe$_2$O$_3$/TiO$_2$ was not substantially altered compared with that of pristine TiO$_2$.

Nevertheless, the average size of the 3.0% Fe$_2$O$_3$/TiO$_2$ was estimated to be approximately 14.6 ± 4.6 nm, resembling TiO$_2$.

### 3.1.2 Crystal structure and Raman spectra

Figure 3(a) shows that the XRD peaks of TiO$_2$ occurring at 25.3°, 37.8°, and 48.0° corresponded to the (101), (004), and (020) planes of anatase. The decoration of Fe$_2$O$_3$ did not give rise to the characteristic peaks at 2θ = 24.1°(012), 33.2°(104), 35.6°(110) for α-Fe$_2$O$_3$ (Maslen et al., 1994), or 36.9°(222), 42.9°(400) for γ-Fe$_2$O$_3$ (Jørgensen et al., 2007) in 0.5-5%Fe$_2$O$_3$/TiO$_2$, implying that Fe$_2$O$_3$ was mainly present in a highly dispersed amorphous phase, or as tiny crystals on the surface of TiO$_2$ that could not be detected by XRD (Fang et al., 2007). However, the decoration of Fe$_2$O$_3$ substantially influenced the diffraction profiles of the TiO$_2$s. For instance, the (020) peak intensity was much higher for Fe$_2$O$_3$/TiO$_2$s than TiO$_2$, as shown in Figure 3(a) and Supplementary Table 1. Additionally, the (020) peak of Fe$_2$O$_3$/TiO$_2$s was much sharper than that of TiO$_2$, which was probably associated with the expansion of TiO$_2$ crystals.
along the [001] direction (Liu et al., 2017), suggesting that Fe$_2$O$_3$ loading could break the strain balance between the top and sublayers of TiO$_2$, thus influencing the epitaxy processes of TiO$_2$ during calcination. Additionally, the full width at half maximum (FWHM) at the 25.3° peak representing the (101) plane was 0.646°, 0.593°, 0.585°, and 0.520° for TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$, respectively. The FWHM was determined according to the Debye-Scherrer equation (Eq. (7)),

$$D = \frac{K\lambda}{\beta\cos\theta}$$  \hspace{1cm} (7)

where D (nm) is the average particulate size and β (without the value) is the FWHM. The particle size of 0.5-7%Fe$_2$O$_3$/TiO$_2$ increased slightly, since the β for the peak corresponding to the Fe$_2$O$_3$/TiO$_2$’s (101) plane was larger than that of TiO$_2$, unveiling that decoration of Fe$_2$O$_3$ slightly promoted the growth in TiO$_2$ size, highly concurring with the size distribution as shown in the TEM images.

Figure 3(b) shows the Raman spectra of TiO$_2$ and 0.5-5% Fe$_2$O$_3$/TiO$_2$. The Raman peaks at 144, 396, 515, and 640 cm$^{-1}$ corresponded to the Eg, B$_{1g}$, B$_{2g}$, and Eg modes of TiO$_2$. The characteristic peaks of Fe$_2$O$_3$ were not present in the Raman patterns of 0.5-5% Fe$_2$O$_3$/TiO$_2$ such as those for α-Fe$_2$O$_3$ occurring at 220 (A$_{1g}$), 243 (E$_g$), 290 (E$_g$), 408 (E$_g$), 611 (E$_g$), 638 (E$_g$) and 1318 cm$^{-1}$(E$_g$) (Kodan et al., 2019), as well as those for γ-Fe$_2$O$_3$ at 350 (E$_g$), 395 (T$_{2g}$), 507 (T$_{2g}$), 670 (A$_{1g}$), and 708 cm$^{-1}$ (A$_{1g}$) (Pawan et al., 2014). The similar Raman patterns between TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$ agreed with the XRD results, revealing that the decorated Fe$_2$O$_3$ on TiO$_2$ formed an amorphous phase or tiny crystallite cell. Nevertheless, the intensities of the 144 and 130 cm$^{-1}$ peaks assigned to the symmetric stretching vibration of the O-Ti-O bonds were relatively
lower for Fe$_2$O$_3$/TiO$_2$ than for the TiO$_2$s, particularly that of 144 cm$^{-1}$ in 5% Fe$_2$O$_3$/TiO$_2$

spectrum, which dropped notably. The lower intensity of the E$_g$ vibration mode of the

Fe$_2$O$_3$/TiO$_2$s probably resulted from the decrease in the O-Ti-O number on the exposed

facet of anatase TiO$_2$ due to the surface cover of amorphous Fe$_2$O$_3$.

### 3.1.3 X-ray photoelectron spectroscopy

Figure 4(a) shows the binding energy of Ti 2p for TiO$_2$ and 3%Fe$_2$O$_3$/TiO$_2$. The

binding energies of 464.4 and 458.5 eV were assigned to Ti$^{4+}$ 2p 1/2 and 3/2 of TiO$_2$,

respectively (Tsai et al., 2013). After the surface loading of Fe$_2$O$_3$, two small subpeaks

emerged at lower binding energies of 463.4 and 457.7 eV, suggesting that the electron

density of the Ti$^{4+}$ 2p orbital increased with the loading of Fe due to the formation of

Fe-O-Ti. The intensity of the Fe 2p peak, as shown on the Y-axis scale in Figure 4(b),

was much smaller than that of Ti$^{4+}$, indicating that the content of surface Fe atoms was

far lower than that of Ti. The main peaks at approximately 710.2 and 724.6 eV were

ascribed to the Fe$^{3+}$ 2p1/2 and 2p3/2 orbitals of Fe$_2$O$_3$, respectively, illustrating that

Fe$^{3+}$ dominated most surface Fe atoms. Additionally, minor shake-up peaks were

present in the range of 713-720 eV, which resulted from an electron transition from a

3d orbital to an empty 4s orbital as the ejection of the Fe 2p electrons (Yin et al., 1974).

### 3.1.4 UV-Visible spectra

Figure 5 illustrates the UV-vis spectra of TiO$_2$ and Fe$_2$O$_3$/TiO$_2$s. Their band gaps

were determined from the intercept between the extrapolated tangent line at the

maximum first-derivative points of the absorption edge and the X-axis. The band gap

of TiO$_2$ was approximately 3.20 eV, which was in agreement with the UV-vis absorption

feature of anatase TiO$_2$. The absorption edge was gradually redshifted with the Fe$_2$O$_3$
content loaded on TiO$_2$. The corresponding band gaps of the 0.5%, 3%, and 5%Fe$_2$O$_3$/TiO$_2$ dropped to 3.14, 2.99, and 2.87 eV, respectively. The UV-vis spectrum of Fe$_2$O$_3$ illustrated a noticeable redshift compared with those of TiO$_2$ and 0.5-5% Fe$_2$O$_3$/TiO$_2$. The adsorption edge occurring at 530-650 nm of the pristine Fe$_2$O$_3$ is probably related to the ligand field transition of 2($^6A_1$)$\rightarrow$(4$^T_1$) (Huang et al., 2017). The band gap was approximately 1.84 eV, approaching 1.88 eV, as reported by Wang et al. (Mansour et al., 2020). Thus, the redshift for 0.5-5.0% Fe$_2$O$_3$/TiO$_2$ compared with TiO$_2$ was principally attributed to the loading of the Fe$_2$O$_3$ cluster.

3.1.5 Photoluminescence spectra and electric properties

Figure 6(a) shows the PL spectra of TiO$_2$ and Fe$_2$O$_3$/TiO$_2$s. The PL emission peaks at 474 nm (2.61 eV) and 500 nm (2.48 eV) were ascribed to the recombination of photoinduced electrons with holes trapped around surface oxygen vacancies (Abdullah et al., 2018). No distinct peak emerged for the Fe$_2$O$_3$/TiO$_2$s, indicating that the decoration of Fe$_2$O$_3$ did not result in new interstitial recombination centers. Nevertheless, the PL intensity decreased with the decorated content of Fe$_2$O$_3$, particularly for 5%Fe$_2$O$_3$/TiO$_2$, illustrating improvement of the separation of photoinduced holes and electrons for the Fe$_2$O$_3$/TiO$_2$s as compared to TiO$_2$.

The simulated EIS patterns of TiO$_2$ and Fe$_2$O$_3$/TiO$_2$s are presented in Figure 6(b). The simulated EIS radius of TiO$_2$ was much larger than those of Fe$_2$O$_3$/TiO$_2$s, illustrating that the decoration of Fe$_2$O$_3$ greatly reduced the interface charge transfer resistance between the electrode and electrolyte, which was probably attributed to the lower electronic resistivity of Fe$_2$O$_3$ (Chang et al., 2014). Moreover, the simulated EIS
decreased with the content of surface Fe$_2$O$_3$, probably owing to an increase in tiny crystals within the Fe$_2$O$_3$, which could significantly reduce the electronic resistivity, although the XRD results did not discern the α- or γ-Fe$_2$O$_3$ crystalline phase (Piva et al., 2016).

The LSV spectra of TiO$_2$ and Fe$_2$O$_3$/TiO$_2$ were measured under UV illumination, as illustrated in Figure 6(c). The photocurrent density of TiO$_2$ was much lower than that of Fe$_2$O$_3$/TiO$_2$ in the applied voltage range of -0.25-0.3 V. Additionally, the photocurrent density of the specimens also increased with the content of Fe$_2$O$_3$. The EIS and LSV results confirmed that the surface decoration of Fe$_2$O$_3$ could promote the separation efficiency of photogenerated electron-hole pairs of TiO$_2$.

### 3.1.6 Electronic structure

The Mott-Schottky plots for TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$ were constructed at 100 Hz using an Ag/AgCl electrode at pH=7.0, as shown in Figure 7(a). The results illustrated that the slope of 1/C$^2$ versus the applied potential was positive for both TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$, demonstrating that they were attributed to n-type semiconductors. Thus, the edges of the flat band (FB) of TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$ are nearly equal to those of the conduction band (CB), as shown in Eq. (8),

\[
\text{CB} \approx \text{FB} \text{ (NHE, pH=7.0)} \quad (8)
\]

The CBs of TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$ were -0.86, -0.91, -1.01, and -1.07 eV, respectively. The corresponding edges of the valence band (VB) could be obtained from the band gap (Eg) and CB as described by Eq. (9),

\[
\text{VB} = \text{CB} + \text{Eg} \quad (9)
\]
The band gaps of TiO\(_2\) and 0.5-5\%Fe\(_2\)O\(_3\)/TiO\(_2\) were 3.20, 3.14, 2.99, and 2.87 eV, respectively. Their VBs were determined to be 2.34, 2.23, 1.98, and 1.80 eV, respectively, as shown in Figure 7(b). The CBs of 0.5-5\%Fe\(_2\)O\(_3\)/TiO\(_2\) were higher than that of TiO\(_2\) (-0.86 eV). This result is possibly related to the realignment of the two Fermi levels of Fe\(_2\)O\(_3\) and TiO\(_2\) after the Fe\(_2\)O\(_3\) and TiO\(_2\) contacted (Liu et al., 2015). As shown in the schematic diagram of the electronic structure of hybrid Fe\(_2\)O\(_3\)/TiO\(_2\) (see Figure 7(c)), the photogenerated electrons transferred from the conduction band of Fe\(_2\)O\(_3\) to that of TiO\(_2\), while the holes moved from the valence band of TiO\(_2\) to Fe\(_2\)O\(_3\). Thus, Fe\(_2\)O\(_3\)/TiO\(_2\) is beneficial for separating the photogenerated electron-hole pairs.

### 3.1.7 EPR

The typical feature of the \(\cdot\)OH signal displays a quartet pattern with an intensity ratio of 1 (g \(\approx\) 1.990): 2 (g \(\approx\) 2.003): 2 (g \(\approx\) 2.012): 1 (g \(\approx\) 2.021) for the TiO\(_2\) and 3\%Fe\(_2\)O\(_3\)/TiO\(_2\), as depicted in Figure 8. The results indicated that a higher intensity was ascertained on the 3\%Fe\(_2\)O\(_3\)/TiO\(_2\) than on TiO\(_2\), implying that the decoration of Fe\(_2\)O\(_3\) was more conducive to increasing \(\cdot\)OH, which was attributed to the efficient photoinduced electron-hole pairs on the interface of Fe\(_2\)O\(_3\) and TiO\(_2\) (Sun et al., 2012).

### 3.2 DFT Calculations

Figure 9(a) shows the effect of the electric field on the free energy of formation of hydroxyl and hydrogen on TiO\(_2\)(010) and Fe\(_2\)O\(_3\)/TiO\(_2\)(010). In the absence of an electric field, energies of 1.56 and 0.70 eV were required for the formation of hydroxyl and hydrogen on TiO\(_2\)(010) and Fe\(_2\)O\(_3\)/TiO\(_2\)(010), respectively, indicating that the decomposition of H\(_2\)O to produce hydroxyl and hydrogen could not proceed spontaneously on these slabs; this decomposition reaction resembled the first reaction
step of the OER for anatase TiO$_2$ in aqueous conditions (Malik et al., 2020).

Nevertheless, for Fe$_2$O$_3$/TiO$_2$(010), the free energy of *-OH + *-H formation decreased by approximately half compared with TiO$_2$. The top Ti-O bond length (2.427 Å) was also reduced to 2.123 Å due to the decoration of amorphous Fe$_2$O$_3$, meaning that atop Fe$_2$O$_3$ on TiO$_2$(010) was more active for splitting H$_2$O than TiO$_2$(010). When a positive external electric field with a strength of 0.05 eV/Å was applied for TiO$_2$(010), the free energy (1.44 eV) of *-OH + *-H formation decreased slightly. It is worth noting that the free energy of formation on Fe$_2$O$_3$/TiO$_2$(010) decreased dramatically to -1.04 eV with a positive electric field, thus spontaneously driving the splitting of H$_2$O into hydroxyl radicals.

To better understand the effect of the electric field on the formation of hydroxyl and hydrogen, the variation in dipole moment ($\mu_0$) of hydroxyl and hydrogen as a whole adsorbed on TiO$_2$(010) and Fe$_2$O$_3$/TiO$_2$(010) was compared. $\mu_0$ is equivalent to the difference between the dipole moment of *-OH + *-H (*-OH) and that of the bare catalyst slab (Deshlahra et al., 2009), which were both obtained from the resulting DFT file. Without an electric field, the dipole moments of *-OH + *-H for TiO$_2$(010) and Fe$_2$O$_3$/TiO$_2$(010) were 0.019 and 0.171 eÅ, respectively, which suggested the more negative charges were distributed on the oxygen atoms of the hydroxyl and on the hydrogen atoms of the Fe$_2$O$_3$/TiO$_2$(010) than those of the TiO$_2$(010). The change in free energy ($\Delta E$, eV) of *-OH + *-H formation due to exposure to an electric field can be predicted by the first-order Stark effect as

$$\Delta E = -\mu_0 \times F$$ (10)
where $\mu_0$ (eÅ) is the dipole moment of the adsorbate without an electric field and $F$ (V/Å) is the strength of an external electric field. The $\Delta E$ was -0.00865 and -0.00097 eV for Fe$_2$O$_3$/TiO$_2$(010) and TiO$_2$(010), respectively, according to Eq. (10), when the electric field was set to 0.05 eV/Å. Although both $\Delta E$ values obtained by Eq. (10) were much smaller than those calculated based on the structure optimization results, the $\Delta E$ of Fe$_2$O$_3$/TiO$_2$(010) was higher than that of TiO$_2$(010); this trend demonstrated that the external electric field in the positive direction favors the formation of hydroxyl and hydrogen on the surface of Fe$_2$O$_3$/TiO$_2$(010). Additionally, the Fe-O bond length (2.077 Å) between the Fe atom and hydroxyl and the O-H bond (1.262 Å) of hydroxyl were much shorter than the corresponding lengths without an electric field, which were 2.123 and 1.274 Å, as shown in Figure 9(a), suggesting that the hydroxyl was bonded more closely to the Fe$_2$O$_3$/TiO$_2$(010) under a positive electric field. It is noted that with the positive electric field, the dissociated hydrogen atom from H$_2$O preferred to interact with one Fe atom at a shorter distance of 2.392 Å, while before the electric field was added, the hydrogen atom was physically connected to one oxygen atom of Fe$_2$O$_3$ at a distance of 2.994 Å. In contrast, a more stable structure was assigned to an unbroken H$_2$O molecule adsorbed on TiO$_2$(010) without the formation of hydroxyl and hydrogen moieties under a positive electric field. The distance between the surface oxygen and surface Ti atom was elongated to 3.208 Å, suggesting that H$_2$O was more difficult to oxidize and split into hydroxyl on TiO$_2$(010) than on Fe$_2$O$_3$/TiO$_2$(010) under a positive electric field.

The effect of a negative electric field on the formation of hydroxyl was also investigated. According to Eq. (10), the predicted $\Delta E$ for the change in the formation
energy would be 0.00865 and 0.00097 eV for TiO$_2$(010) and Fe$_2$O$_3$/TiO$_2$(010) under a field strength of -0.05 V/Å, indicating that an electric field in the negative direction was not beneficial for splitting H$_2$O compared with the positive electric field. The formation free energies of the hydroxyl and hydrogens were also determined based on structure optimization, as shown in Figure 9(a), which were 1.01 eV for TiO$_2$(010) and -0.22 eV for Fe$_2$O$_3$/TiO$_2$(010). They were much lower than those under a positive electric field, demonstrating that a positive electric field was more effective than a negative electric field to promote hydroxyl production. Additionally, the atomic distance between the oxygen atom of the hydroxyl and the Fe or Ti atom, and the distance between the dissociated hydrogen atom and the Fe atom became longer under a negative electric field, as shown in Figure 9(a).

When the detached hydrogen atom of H$_2$O was lost under the gaseous flow, the production of hydroxyl could not still proceed spontaneously regardless of the direction in which the electric field was applied, as illustrated in Figure 9(b). For instance, the free energy of *-OH formation for TiO$_2$(010) was 1.759 eV, while it was 1.445 eV for Fe$_2$O$_3$/TiO$_2$(010). The free energy of *-OH formation alone increased to 2.927 eV and 2.423 eV for TiO$_2$(010) and Fe$_2$O$_3$/TiO$_2$(010), respectively, when a positive electric field was added. Likewise, the negative electric field resulted in free energies of 1.445 eV and 0.7817 eV. The results implied that the hydrogen atom that was dissociated from the H$_2$O molecule was more likely to remain on the TiO$_2$(010) and Fe$_2$O$_3$/TiO$_2$(010) than to be taken away by flow gases.

Figure 10 illustrates the electric field's influence on the density of states of
Fe$_2$O$_3$/TiO$_2$ and Fe$_2$O$_3$/TiO$_2$(010) with the adsorbed hydroxyl and hydrogen. The band gap of Fe$_2$O$_3$/TiO$_2$ was approximately 2.30 eV, as shown in the total density state Fe$_2$O$_3$/TiO$_2$ in Figure 10(a). No distinct energy state emerged within the band gap of Fe$_2$O$_3$/TiO$_2$, concurring with the PL profile of Fe$_2$O$_3$/TiO$_2$. Additionally, the projected density state showed that the profile of Fe 3d mainly resided on the edge of the conduction band. Figure 10(b)-(d) shows that the band gaps of Fe$_2$O$_3$/TiO$_2$(010) with adsorbed hydroxyl and hydrogen with and without an electric field were all 2.30 eV, suggesting the external electric field did not change the magnitude of the band gap of Fe$_2$O$_3$/TiO$_2$(010). However, without the electric field, a few energy states were distributed within the band gap for the Fe$_2$O$_3$/TiO$_2$(010) that had adsorbed hydroxyl and hydrogen; these energy states were mainly derived from the interaction between Fe 3d and the sp hybrid orbitals of the surface hydrogen and oxygen atoms, indicating a strong bond formed between the Fe and atom oxygen and hydrogen, as shown in Figure 10(b). However, once the positive electric field was applied to the Fe$_2$O$_3$/TiO$_2$(010) with adsorbed hydroxyl and hydrogen, most of the band gap density states vanished, particularly at the higher energy level. Only two states closer to the valance band margin remained, revealing that the bond energy between the Fe3d and hybrid OH orbitals became more stable under a positive electric field, thus promoting the bond to be much stronger (see Figure 10(c)). In contrast, if a negative electric field was added, the location and number of the energy state remained almost unchanged, suggesting that a negative direction less influenced the bond of the Fe 3d and OH hybrid orbitals, as illustrated in Figure 10(d).
The Fermi level of Fe$_2$O$_3$/TiO$_2$, which is defined herein as the top of the valence band, was -0.72 eV, while that of Fe$_2$O$_3$/TiO$_2$+ hydroxyl + hydrogen was 1.12 eV, as shown in Figure 10(a) and (b). The remarkable shift of the Fermi level towards the conduction band margin for Fe$_2$O$_3$/TiO$_2$+ hydroxyl + hydrogen resulted from the new mid-gap state of the interaction between Fe 3d and atop hydrogen and oxygen atoms. When an external positive electric field was applied to the slab, the Fermi level (0.09 eV) decreased markedly in comparison to that without an electric field, as shown in Figure 10(c). This implied that the positive electric field attracted more positive charges that accumulated on the surface of Fe$_2$O$_3$/TiO$_2$, thus decreasing the Fermi level (Tiewcharoen et al., 2017), which was beneficial for splitting H$_2$O. In contrast, under the negative electric field, the Fermi level shifted towards a much higher energy level, reaching 1.40 eV, suggesting that the negative electric field resulted in more negative electric charges distributed on the surface, thus notably lifting the Fermi level, but decreasing the formation of hydroxyl and hydrogen.

### 3.3 Photoelectric Activity

The photocatalytic and photoelectric removal efficiencies of CHOH by neat TiO$_2$, and 0.5-5.0%Fe$_2$O$_3$/TiO$_2$ were determined without the addition of H$_2$O, as illustrated in Figure 11. Figure 11(a) displays that without UV irradiation, the removal efficiency by neat TiO$_2$ was approximately 64%, suggesting that even if no UV was exploited, TiO$_2$ could adsorb CHOH via the interactions between the surface Ti of TiO$_2$ and the oxygen atom of CHOH, as well as the surface oxygen and carbon atom of CHOH. Then, the two hydrogen atoms of CHOH were further separated (Wu et al., 2018). The isolated
fragments of C-O and H then reacted with O\textsubscript{2} to produce CO\textsubscript{2} and H\textsubscript{2}O. The Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2}s had a much higher removal efficiency than neat TiO\textsubscript{2}, reaching more than 80%, particularly for 3%Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2}, which had the highest removal efficiency of 86% among these catalysts. The enhancement of the removal efficiency by Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} was probably due to the stronger interaction between the surface Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} and CHOH than between TiO\textsubscript{2} and CHOH, whose adsorption energies were determined to be -1.49 and -1.08 eV, respectively, as illustrated in Figure S-1. When an external voltage of 150 V was introduced into the reactor, the removal efficiencies were nearly the same as those without the addition of applied voltage for both TiO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2}s, conveying that an external voltage of 150 V on the catalysts could not directly influence the interaction between CHOH and TiO\textsubscript{2} (Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2}s).

Figure 11(b) shows that when the UV irradiation was added, the photocatalytic removal efficiencies of CHOH were approximately 68% and 85-97% by TiO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2}s, respectively, an overall increase of 5-10% compared with their removal efficiency without UV irradiation. The increase in the removal efficiencies was attributed to the oxidation of CHOH by hydroxyl radicals derived from the photoinduced holes with surface adsorbed H\textsubscript{2}O, as described by Eqs. (11)-(12),

\[
\cdot\text{OH} + \text{CHOH} \rightarrow \text{H}_2\text{O} + \text{CHO}^- \quad (11)
\]

\[
2\text{CHO}^- + \text{O}_2 \rightarrow \text{HCOOH} + \text{CO}_2 \quad (12)
\]

Additionally, the increment contributed by Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2}s was 7-10%, much higher than 5% by TiO\textsubscript{2}, owing to the interfacial transportation of photoinduced electrons and a lower electrical impedance of Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2}. When the electric field and UV irradiation...
were simultaneously applied to the reaction system, the removal efficiencies of CHOH were not further enhanced, suggesting that the interaction between the surface Ti and Fe atoms and CHOH could not be influenced by such a relatively low electric field, even if electrons had moved freely within their conduction band.

When a mixed flue gas with a relative humidity of 50% was supplied into the reactor, the removal efficiencies of CHOH by TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$ under irradiation or not were all depressed compared to those without H$_2$O interference, as illustrated in Figure 12(a) and (b), indicating that H$_2$O caused competitive adsorption with CHOH. Nevertheless, either the catalytic (41%) or photocatalytic (51%) removal efficiencies of CHOH by TiO$_2$ were lower than 54-60% and 70-80% by 0.5-5%Fe$_2$O$_3$/TiO$_2$, implying that the decoration of Fe$_2$O$_3$ can relieve H$_2$O inhibition to some degree. When an external voltage of 150 V was introduced, the catalytic removal efficiencies of CHOH by TiO$_2$ and Fe$_2$O$_3$/TiO$_2$ were still not enhanced without irradiation. Noticeably, once UV irradiation was added, their photocatalytic activity was markedly promoted, and the removal efficiencies had increased by approximately 5% and 10% for TiO$_2$ and Fe$_2$O$_3$/TiO$_2$, respectively. Consistent with the DFT results, the combined effect of the applied electric field and UV irradiation on the Fe$_2$O$_3$/TiO$_2$ was more beneficial for enhancing the removal efficiency of CHOH than TiO$_2$. Additionally, the pH of the effluent gas during the photoelectrical catalytic degradation of CHOH under a relative humidity of 50% was sampled at the outlet and measured to be neutral, experimentally revealing that the protons were not taken away by the carrier gases with the external electric field. Additionally, after the reaction finished, we observed that the
Fe$_2$O$_3$/TiO$_2$ retained the same faint, slightly yellowish as it had when it was fresh, revealing that the electric field-assisted photooxidation of CHOH on Fe$_2$O$_3$/TiO$_2$ does not cause an accumulation of photogenerated electrons or holes on the Fe$_2$O$_3$/TiO$_2$, therefore avoiding drastic changes in its structure. The photogenerated holes were principally distributed on Fe$_2$O$_3$, which finally participated in the formation of hydroxyl radicals to oxidize CHOH. The photogenerated electrons trapped by the Ti$^{3+}$ had different reaction pathways, dominantly including a) reacting with O$_2$ to produce ·O$_2^-$ for CHOH oxidation or directly participating in the attachment of the carbonyl of CHOH to Ti$^{3+}$ (Cremer et al., 2014), or (b) moving towards the positive electrode of the input DC device, particularly for those produced by the TiO$_2$ or Fe$_2$O$_3$/TiO$_2$ nanogranules having physical contact with the mesh plates.

Additionally, the photoelectrical removal efficiencies of CHOH under different relative humidity (20-80%) conditions were much higher than their photooxidation efficiency of CHOH, as illustrated in Figure S-2. Therefore, combining the DFT and EPR results, the resistance to the competitive adsorption of H$_2$O was attributed to the more hydroxyl radicals were photoelectrical splitting of H$_2$O molecules.

By adjusting the distance between the two mesh plates to change the electric field’s strength, we investigated the relationship between the applied electric field’s strength and the incremental change in removal efficiency and rate compared to those of the samples without an applied electric field, as shown in Figure 13(a). The results illustrated that the removal efficiencies of CHOH by 3%Fe$_2$O$_3$/TiO$_2$ were 74.3 ± 1.83%, 76.8 ± 1.57%, 86.8 ± 1.30%, and 89.9 ± 1.57%, under electric field strengths of 0, 2500,
5000, and 7500 V/m, respectively, suggesting an increase in the removal efficiencies with the electric field strength. However, the relationship between the increments of removal rate and the electric field magnitude was not a good linear relationship, as illustrated in Figure 13(b). The results implied that the formation of free energy of hydroxyl depends on the electric field strength, and other reaction parameters such as the energy barrier are possibly influenced.

The removal rates of CHOH with various low levels of power input were compared in Figure 14. Without competitive adsorption of H₂O, 15-W lump irradiation could improve the removal rates by 7% and 10%, reaching maximum removal rates of 2954 and 4129 ng/g/min for TiO₂ and 3% Fe₂O₃/TiO₂, respectively, while the 5-W electric field contributed little to the enhancement. Under a relative humidity of 50%, the removal rates of CHOH significantly dropped for both TiO₂ and Fe₂O₃/TiO₂ without any input energy. However, after introducing 15-W irradiation, the removal rates of CHOH increased by 26% and 24% for TiO₂ and 3% Fe₂O₃/TiO₂, respectively. Moreover, the 5-W electric field was further added, the removal rates increased further by 13% and 23%, particularly for 3% Fe₂O₃/TiO₂, which had nearly the same efficacy as the 15-W input power. Additionally, the final photoelectrocatalytic oxidation rate reached 3747 ng/g/min for 3% Fe₂O₃/TiO₂, which approached its highest H₂O-free removal rate of 4130 ng/g/min. Therefore, a total of 20-W low-power input was verified to effectively resist the inhibition of H₂O on the CHOH removal by 3%Fe₂O₃/TiO₂.

Conclusions

The photoelectric removal of CHOH by TiO₂ and 0.5-5.0%Fe₂O₃/TiO₂ in a humid
environment was theoretically and experimentally investigated in this study. The DFT results demonstrated that a positive electric field was beneficial for splitting H₂O into a hydroxyl and a hydrogen atom on TiO₂ and Fe₂O₃/TiO₂ than a negative electric field, and without any electric fields. The Fe₂O₃ decoration can enhance the formation of hydroxyls than TiO₂ under the positive electric field. The DOS result showed that the bond energy of Fe 3d orbital and the sp hybrid orbital of OH decreased to a lower energy state, thus leading to the hydroxyl formation. Additionally, it was favorable for the dissociated hydrogen atom from the H₂O molecule to attach to the surface of catalysts rather than being transported by flow gas. The experimental results demonstrated that the addition of a low-energy external field could not directly improve the removal efficiency of CHOH but could relieve the adsorptive adsorption of the H₂O molecule, concurring with the DFT results. Fe₂O₃/TiO₂ exhibited a higher H₂O resistance than TiO₂, which was attributed to more hydroxyl radicals produced on Fe₂O₃/TiO₂. In the future, we will focus on the influence of a high-voltage electric field on the photooxidation of CHOH by more active modified TiO₂, and investigate the direct influence of dipole moment of CHOH, adsorption of CHOH.

Acknowledgment

This study was performed under the auspices of the Xiamen Science & Technology Plan, under the contract number of 3502Z20183026, the National Key Research and Development Program (2019YFC0214305), and the National Natural Science Foundation of China, China, (Grant No. 51908230). The authors are grateful to their financial supports in order to accomplish this study. The supplemented materials have
other 1 table and 2 figures.
Ethics approval and consent to participate: Not applicable

Consent for publication: Not applicable

Competing interests: The authors declare that they have no competing interests

Availability of data and materials: Not applicable

Funding: This study was performed under the auspices of the Xiamen Science & Technology Plan, under the contract number of 3502Z20183026, the National Key Research and Development Program (2019YFC0214305), and the National Natural Science Foundation of China, China, (Grant No. 51908230). W. Xia gratefully acknowledge the support from the Department of Civil & Environmental Engineering at North Dakota State University.

Authors' contributions: Not applicable

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References

Abdullah SA, Sahdan MZ, Nafarizal N, Saim H, Bakri AS, Rohaida CHC, Adriyanto F, Sari Y (2018) Photoluminescence study of trap-state defect on TiO\textsubscript{2} thin films at different substrate temperature via RF magnetron sputtering. J Phys: Conf Ser 995: 012067.

Adawiah MARa, Zaidon A, Izreen FAN, Bakar ES, Hamami SM, Paridah MT (2012) Addition of urea as formaldehyde scavenger for low molecular water phenol formaldehyde-treated compeg wood. J Tropical Forest Sci 24: 348-357.

Chang KC, Ji WF, Lai MC, Hsiao YR, Hsu CH, Chuang TL, Wei Y, Yeh JM, Liu WR (2014) Synergistic effects of hydrophobicity and gas barrier properties on the anticorrosion property of PMMA nanocomposite coatings embedded with graphene nanosheets. Polym Chem 5: 1049-1056.

Chen BB, Zhu XB, Crocker M, Wang Y, Shi C (2014) FeO\textsubscript{x}-supported gold catalysts for catalytic removal of formaldehyde at room temperature. Appl Catal, B 154-155: 73-81.

Ciancio R, Carlino E, Rossi G, Aruta C, Uccio USd, Vittadini A, Selloni A (2012) Magneli-like phases in epitaxial anatase TiO\textsubscript{2} thin films. Phys Rev B 86: 104110.

Cremer T, Jensen SC, Friend CM (2014) Enhanced photo-oxidation of formaldehyde on highly reduced o-TiO\textsubscript{2}(110). J Phys Chem C 118: 29242-29251.

Deshlahra P, Wolf EE, Schneider WF (2009) A periodic density functional theory analysis of CO chemisorption on Pt(111) in the presence of uniform electric fields. J Phys Chem A 113: 4125-4133.

Ding CS, Nohira T, Hagiwara R (2017) TiO\textsubscript{2}-Fe\textsubscript{2}O\textsubscript{3} nanocomposites as high-capacity negative electrode materials for rechargeable sodium-ion batteries. Sustainable Energy & Fuels 1: 371-376.

Ding JJ, Rui ZB, Lyu PT, Liu YL, Liu XK, Ji HB (2018) Enhanced formaldehyde oxidation performance over Pt/ZSM-5 through a facile nickel cation modification. Appl Sur Sci 457: 670-675.

Duan ZY, Henkelman G (2019) Theoretical resolution of the exceptional oxygen reduction activity of Au(100) in alkaline media. ACS Catal 9: 5567-5573.

Fang J, Bi XZ, Si DJ, Jiang ZQ, Huang WX (2007) Spectroscopic studies of interfacial structures of CeO\textsubscript{2}-TiO\textsubscript{2} mixed oxides. Appl Surf Sci 253: 8952-8961.

Filhol JS, Neurock M (2006) Elucidation of the electrochemical activation of water over Pd by first principles. Angew Chem Int Ed 45: 402-406.

Guo JH, Lin CX, Jiang CJ, Zhang PY (2019) Review on noble metal-based catalysts for formaldehyde oxidation at room temperature. Appl Surf Sci 475: 237-255.

Huang RK, Liang RW, Fan HM, Ying SM, Wu L, Wang XX, Yan GY (2017) Enhanced photocatalytic fuel denitrification over TiO\textsubscript{2}/α-Fe\textsubscript{2}O\textsubscript{3} nanocomposites under visible light irradiation. Sci Rep 7: 7858.

Huang ZW, Du YY, Zhang J, Wu XM, Shen HZ, Jing GH (2019) Exceptional activity over the submonolayer MoO\textsubscript{3} motif on TiO\textsubscript{2} for nitrogen oxide emission abatement. Environ Sci Technol 53: 5309-5318.
Jörg N, Matthias S (1992) Adsorbate-substrate and adsorbate-adsorbate interactions of Na and K adlayers on Al(111). Phys Rev B 46: 16067-16080.

Jørgensen JE, Mosegaard L, Thomsen LE, ensen JR, Hanson JC (2007) Formation of $\gamma$-$\text{Fe}_2\text{O}_3$ nanoparticles and vacancy ordering: An in situ X-ray powder diffraction study. J Solid State Chem 180: 180-185.

Kim KH, Jahan SA, Lee JT (2011) Exposure to formaldehyde and its potential human health hazards. J Environ Sci Health Part C-Environ Carcinog Ecotoxicol Rev 29: 277-299.

Kodan N, Agarwal K, Mehta BR (2019) All-oxide $\alpha$-$\text{Fe}_2\text{O}_3$/H:TiO$_2$ heterojunction photoanode: A platform for stable and enhanced photoelectrochemical performance through favorable band edge alignment. J Phys Chem C 123: 3326-3335.

Li R, Huang Y, Zhu DD, Ho WK, Lee SC, Cao JJ (2020) A Review of $\text{Co}_3\text{O}_4$-based Catalysts for Rormaldehyde Oxidation at Low Temperature: Effect parameters and reaction mechanism. Aerosol Sci Eng 4: 147-168.

Liang WJ, Li J, Jin YQ (2012) Photo-catalytic degradation of gaseous formaldehyde by TiO$_2$/UV, Ag/TiO$_2$/UV and Ce/TiO$_2$/UV. Build Environ 51: 345-350.

Liu J, Yang SL, Wu W, Tian QY, Cui SY, Dai ZG, Ren F, Xiao KH, Jiang CZ (2015) 3D flowerlike $\alpha$-$\text{Fe}_2\text{O}_3$@TiO$_2$ core-shell nanostructures: general synthesis and enhanced photocatalytic performance. ACS Sustain Chem Eng 3:2975-2984.

Mansour H, Omri K, Bargougui R, Ammar S (2020) Novel $\alpha$-$\text{Fe}_2\text{O}_3$/TiO$_2$ nanocomposites with enhanced photocatalytic activity. Appl Phys A 126: 151.

Maslen EN, Strletova VA, Strletova NR, N. Ishizawa (1994) Synchrotron X-ray study of the electron density in $\alpha$-$\text{Fe}_2\text{O}_3$. Acta Crystallographica Section B 50: 435-441.

Miao L, Wang JL, Zhang PY (2019) Review on manganese dioxide for catalytic oxidation of airborne formaldehyde. Appl Surf Sci 466: 441-453.

Moniz SJ, Shevlin SA, An X, Guo ZX, Tang Jw (2014) $\text{Fe}_2\text{O}_3$/TiO$_2$ nanocomposites for enhanced charge separation and photocatalytic activity. Chem-A Europe J 20: 15571-15579.

Nie LH, Yu JG, Jaroniec M, Tao FF (2016) Room-temperature catalytic oxidation of formaldehyde on catalysts. Catal Sci Technol 6: 3649-3669.

Nørskov JK, Rossmeisl J, Logadottir A, Lindqvist J, Kitchin JR, Bligaard T, Jónsson H (2004) Origin of the overpotential for oxygen reduction at a fuel-cell cathode. J Phys Chem B 108: 17886-17892.

Pan J, Liu G, Lu GQ, Cheng HM (2011) On the true photoreactivity order of {001},
{010}, and {101} facets of anatase TiO\textsubscript{2} crystals. Angew Chem Int Ed 50: 2133-2137.

Pawan K, Heung NL, Rajesh K (2014) Synthesis of phase pure iron oxide polymorphs thin films and their enhanced magnetic properties. J Mater Sci: Mater Electron 25: 4553-4561.

Piva DH, Piva RH, Venturini J, Ramon J, Caldas V, Morelli MR, Bergmann CP (2016) Effect of Fe\textsubscript{2}O\textsubscript{3} content on the electrical resistivity of aluminous porcelain applied to electrical insulators. Ceram Int 42: 5045-5052.

Shen Hz, Lin MJ, Wang LD, Huang ZW, Wu XM, Jiang XQ, Li Q, Chen CL, Zhao JX, Jing GH, Yuan CS (2021) Experimental and theoretical investigation of the enhancement of the photo-oxidation of Hg\textsuperscript{0} by CeO\textsubscript{2}-modified morphology-controlled anatase TiO\textsubscript{2}. J Hazard Mater 406: 124535.

Shim SH, Bengtson A, Morgan D, Sturhahn W, Catalli K, Zhao JY, Lerche M, Prakapenka V (2009) Electronic and magnetic structures of the postperovskite-type Fe\textsubscript{2}O\textsubscript{3} and implications for planetary magnetic records and deep interiors. Proc Nat Acad Sci 106: 5508.

Sun Q, Leng WH, Li Z, Xu Y (2012) Effect of surface Fe\textsubscript{2}O\textsubscript{3} clusters on the photocatalytic activity of TiO\textsubscript{2} for phenol degradation in water. J Hazard Mater 229-230: 224-232.

Sun S, Ding JJ, Bao J, Gao C, Qi ZM, Li CX (2010) Photocatalytic oxidation of gaseous formaldehyde on TiO\textsubscript{2}: An in-situ DRIFTS study. Catal Lett 137: 239-246.

Tang XJ, Bai Y, Duong A, Smith MT, Li LY, Zhang LP (2009) Formaldehyde in China: Production, consumption, exposure levels, and health effects. Environ Int 35: 1210-1224.

Tasbihi M, Bendyna JK, Notten P, Hintzen H (2015) A short review on photocatalytic degradation of formaldehyde. J Nanosci Nanotech 15: 6386-6396.

Tiewcharoen S, Warakulwit C, Lapeyre V, Garrigue P, Fourier L, Elissalde C, Buffière S, Legros P, Marion Gayot, Limtrakul J, Kuhn A (2017) Anisotropic metal deposition on TiO\textsubscript{2} particles by electric-field-induced charge separation. Angew Chem Int Ed 56: 11431-11435.

Tsai CY, Hsi HC, Kuo TH, Chang YM, Liou JH (2013) Preparation of Cu-doped TiO\textsubscript{2} photocatalyst with thermal plasma torch for low-concentration mercury removal. Aerosol Air Qual Res 13: 639-648.

Valdés Á, Qu ZW, Kroes GJ, Rossmeisl J, Nørskov JK (2008) Oxidation and photocatalysis of gaseous formaldehyde on TiO\textsubscript{2} surface. J Phys Chem C 112: 9872-9879.

Wang J, Wang JT, Wu XY, Zhang GK (2017) Pt-TiO\textsubscript{2} microspheres with exposed {001} facets for degradation of formaldehyde in air: Formation mechanism and enhanced visible light photocatalytic activity. Mater Res Bull 96: 262-269.

Wang S, Lian JS, Zheng WT, Jiang Q (2012) Photocatalytic property of Fe doped anatase and rutile TiO\textsubscript{2} nanocrystal particles prepared by sol-gel technique. Appl Surf Sci 263: 260-265.

Wang YS, Wang SR, Zhang HX, Gao XL, Yang JQ, Wang LQ (2014) Brookite TiO\textsubscript{2} decorated α-Fe\textsubscript{2}O\textsubscript{3} nanoheterostructures with rod morphologies for gas sensor
Wu GF, Zhao CH, Guo CQ, Chen JH, Zhang YB, Li YQ (2018) DFT study on the interaction of TiO$_2$ (001) surface with HCHO molecules. Appl Surf Sci 428: 954-963.

Yang S, Zhu ZX, Wei F, Yang XD (2017) Enhancement of formaldehyde removal by activated carbon fiber via in situ growth of carbon nanotubes. Build Environ 126: 27-33.

Yin L, Adler I, Tsang T, Matienzo LJ, Grim SO (1974) Paramagnetism and shake-up satellites in X-ray photoelectron spectra. Chem Phys Lett 24: 81-84.

Yu JG, Wang SH, Low JX, Xiao W (2013) Enhanced photocatalytic performance of direct Z-scheme g-C$_3$N$_4$–TiO$_2$ photocatalysts for the decomposition of formaldehyde in air. Phys Chem Chem Phys 15: 16883-16890.

Zhang GX, Sun ZM, Wei Y, Ma R, Zheng S (2017) Synthesis of nano-TiO$_2$/diatomite composite and its photocatalytic degradation of gaseous formaldehyde. Appli Surf Sci 412: 105-112.
Figure captions

Figure 1. Diagram of the photoelectrical catalytic reaction system.

Figure 2. Morphology of TiO$_2$ (a) SEM, (b)-(c) TEM, (d) size distribution, and 3%Fe$_2$O$_3$/TiO$_2$ (e) SEM, (f)-(g) TEM, (h) size distribution.

Figure 3. (a) XRD and (b) Raman patterns of TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$.

Figure 4. Binding energies of (a) Ti 2p$_{1/2}$, Ti 2p$_{3/2}$ for TiO$_2$ and 3%Fe$_2$O$_3$/TiO$_2$, and (b) Fe 2p$_{1/2}$.

Figure 5. UV-Visible spectra of TiO$_2$, 0.5-5%Fe$_2$O$_3$/TiO$_2$, and Fe$_2$O$_3$.

Figure 6. (a) PL spectra, (b) simulated EIS, and (c) LSV patterns of TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$.

Figure 7. (a) Mott-Schottky plots of TiO$_2$, 0.5-5%Fe$_2$O$_3$/TiO$_2$, and Fe$_2$O$_3$ at 100 Hz using an Ag/AgCl electrode at pH=7.0, (b) electronic structure of TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$, (c) schematic diagram of photogenerated electron-hole pairs transferring at the interface of Fe$_2$O$_3$/TiO$_2$, and Fe$_2$O$_3$.

Figure 8. EPR patterns of TiO$_2$ and Fe$_2$O$_3$/TiO$_2$.

Figure 9. Free energy of formation of (a) slab + hydroxyl + H, and (b) slab + hydroxyl.

Figure 10. Projected density of state for bare Fe$_2$O$_3$/TiO$_2$ (a), Fe$_2$O$_3$/TiO$_2$ + hydroxyl + hydrogen (b) without an electric field, (c) Fe$_2$O$_3$/TiO$_2$ + hydroxyl + hydrogen with a positive electric field, and (d) with a negative electric field, respectively. Dashed lines denote the Fermi level.

Figure 11. Removal efficiency of CHOH by neat TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$ without H$_2$O, (a) in the absence and (b) presence of UV irradiation.

Figure 12. Removal efficiency of CH$_2$O by neat TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$ at a relative humidity of 50%, (a) in the absence and (b) presence of UV irradiation.

Figure 13. (a) Removal efficiency of CHOH by 3%Fe$_2$O$_3$/TiO$_2$, and (b) increment of the removal rates of CHOH by 3%Fe$_2$O$_3$/TiO$_2$ at a relative humidity of 50% under different strengths of electric field.

Figure 14. Removal rate of CHOH with different energy input (a) without H$_2$O, and (b) with H$_2$O.
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Potential (V) vs Ag/AgCl, pH = 7

(a) Graph showing the relationship between potential and density of states.

(b) Conduction and Valence Band diagram with specific energy levels and materials.

- 5% Fe₂O₃/TiO₂
- 3% Fe₂O₃/TiO₂
- 0.5% Fe₂O₃/TiO₂
- TiO₂

Energy levels:
- TiO₂: 2.34 eV
- 0.5% Fe₂O₃/TiO₂: 2.23 eV
- 3% Fe₂O₃/TiO₂: 1.98 eV
- 5% Fe₂O₃/TiO₂: 1.80 eV

Potential values:
- -1.07 V
- -1.01 V
- -0.91 V
- -0.86 V
- -0.8 V
- -0.7 V
- -0.6 V
- -0.5 V
- -0.4 V

Graphical analysis and comparison of materials with different Fe₂O₃ concentrations.
Figure 7. (a) Mott-Schottky plots of TiO$_2$, 0.5-5\%Fe$_2$O$_3$/TiO$_2$, and Fe$_2$O$_3$ at 100 Hz using an Ag/AgCl electrode at pH=7.0, (b) electronic structure of TiO$_2$ and 0.5-5\%Fe$_2$O$_3$/TiO$_2$, (c) schematic diagram of photogenerated electron-hole pairs transferring at the interface of Fe$_2$O$_3$/TiO$_2$, and Fe$_2$O$_3$. 
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Figure 10. Projected density of state for bare Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} (a), Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} + hydroxyl + hydrogen (b) without an electric field, (c) Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} + hydroxyl + hydrogen with a positive electric field, and (d) with a negative electric field, respectively. Dashed lines denote the Fermi level.
Figure 11. Removal efficiency of CHOH by neat TiO\textsubscript{2} and 0.5-5\%Fe\textsubscript{2}O\textsubscript{3}/TiO\textsubscript{2} without H\textsubscript{2}O, (a) in the absence and (b) presence of UV irradiation. The overall flow rate of 700 mL/min, influent CHOH concentration of 1.50 ppm, the mass of 0.3 g catalysts, the power of 15 W for UV irradiation, and 5 W for the electric field.
Figure 12. Removal efficiency of CH$_2$O by neat TiO$_2$ and 0.5-5%Fe$_2$O$_3$/TiO$_2$ at a relative humidity of 50%, (a) in the absence and (b) presence of UV irradiation. The overall flow rate of 700 mL/min, influent CHOH concentration of 1.50 ppm, the mass of 0.3 g catalysts, the power of 15 W for UV irradiation, and 5 W for the electric field.
Figure 13. (a) Removal efficiency of CHOH by 3%Fe₂O₃/TiO₂, and (b) increment of the removal rates of CHOH by 3%Fe₂O₃/TiO₂ at a relative humidity of 50% under different strengths of electric field. The overall flow rate of 700 mL/min, influent CHOH concentration of 1.50 ppm, the mass of 0.3 g catalysts, the power of 15 W for UV irradiation, and 5 W for the electric field.
Figure 14. Removal rate of CHOH with different energy input (a) without H$_2$O, and (b) with H$_2$O.

(a) Removal rate (ng/(g/min)) of CHOH with different energy input (a) without H$_2$O, and (b) with H$_2$O.

(b) Removal rate (ng/(g/min)) of CHOH with different energy input (a) without H$_2$O, and (b) with H$_2$O.
Figures

Figure 1

Diagram of the photoelectrical catalytic reaction system.

Figure 2
Figure 3

(a) XRD and (b) Raman patterns of TiO2 and 0.5-5%Fe2O3/TiO2.
Figure 4

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Figure 6
(a) PL spectra, (b) simulated EIS, and (c) LSV patterns of TiO2 and 0.5-5%Fe2O3/TiO2.
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Projected density of state for bare Fe2O3/TiO2 (a), Fe2O3/TiO2 + hydroxyl + hydrogen (b) without an electric field, (c) Fe2O3/TiO2 + hydroxyl + hydrogen with a positive electric field, and (d) with a negative electric field, respectively. Dashed lines denote the Fermi level.

Figure 11
Removal efficiency of CHOH by neat TiO2 and 0.5-5%Fe2O3/TiO2 without H2O, (a) in the absence and (b) presence of UV irradiation.
Figure 12

Removal efficiency of CH2O by neat TiO2 and 0.5-5%Fe2O3/TiO2 at a relative humidity of 50%, (a) in the absence and (b) presence of UV irradiation.

Figure 13

(a) Removal efficiency of CHOH by 3%Fe2O3/TiO2, and (b) increment of the removal rates of CHOH by 3%Fe2O3/TiO2 at a relative humidity of 50% under different strengths of electric field.
Figure 14

Removal rate of CHOH with different energy input (a) without H2O, and (b) with H2O.

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