Retracted: The Fabrication of Magnetically Recyclable La-Doped TiO₂/Calcium Ferrite/Diatomite Composite for Visible-Light-Driven Degradation of Antibiotic and Disinfection of Bacteria

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Abstract

Environmental Engineering Science officially retracts the paper entitled, “The Fabrication of Magnetically Recyclable La-Doped TiO₂/Calcium Ferrite/Diatomite Composite for Visible-Light-Driven Degradation of Antibiotic and Disinfection of Bacteria,” by Qiong Wu and Zhaohong Zhang (Environ Eng Sci. 2020;37(2):109–119. (doi: 10.1089/ees.2019.0202) due to the lead author, Dr. Qiong Wu, falsely and inappropriately adding Dr. Zhaohong Zhang as a co-author.

Dr. Zhaohong Zhang contacted the journal and requested to be removed as an author of the published paper. The publisher referred the complaint to the authors’ institution (Liaoning University, Shenyang, P.R. China) and they initiated an inquiry. The results of that inquiry determined that Dr. Wu dishonestly added Dr. Zhang to the paper without Dr. Zhang’s knowledge or permission. This is considered a serious violation of the standard and proper protocols of scientific publishing, and therefore, the journal officially retracts the paper.

The Editor and Publisher of *Environmental Engineering Science* are committed to upholding all requirements of scientific peer review and publishing and will not tolerate any improprieties.

Keywords: calcium ferrite; diatomite; La doped; magnetic recyclable; oxytetracycline

Introduction

OVER THE PAST few decades, one typical antibiotic, oxytetracycline (OTC), has been widely used in treating human and animal infections. The residue of OTC has been detected in water environment, resulting in the formation of antibiotic resistance bacteria, which pose great threats to both human and livestock (Chen *et al.*, 2018). Besides, conventional water treatment could hardly eliminate antibiotic residue, due to its stable chemical property.

Recently, new methods dealing with OTC residues have been proposed, such as photocatalysis and Fenton and ozonation processes (Van *et al.*, 2019), which have received tremendous attention since they can effectively mineralize OTC molecules into inorganic substances (Qiang *et al.*, 2018). TiO₂-based photocatalysis presented good de-

composition rate toward OTC under ultraviolet (UV) light (Chen and Liu, 2017a; Qiang *et al.*, 2018). The shortcoming of this method is that, UV light takes up only 4% of solar light spectrum. Thus, the development of visible-light-active photocatalyst is increasingly required.

The doping of TiO₂ to transform it into visible-light-driven photocatalyst has been reported as one efficient method (Sun *et al.*, 2019). Among various elements, rare-earth element doping has been favored due to its unique atomic structure. La doping narrows the bandgap of TiO₂ and extends the light absorption into visible light region (Liu *et al.*, 2016). Moreover, La dopant in TiO₂ acts as electron acceptor during photocatalytic reaction, due to the La³⁺/La⁴⁺ redox couple. The redox couple attracts photo-induced electrons, hindering the recombination of charge carriers and enhancing photocatalytic activity.

Many ferrite-based semiconductors present photocatalytic activity under visible light. Among these, calcium ferrite (CaFe₂O₄) has been favored due to its relatively narrower bandgap (1.85 eV), while the bandgap value of anatase phase TiO₂ is 3.20 eV (Zhang and Wang, 2014; Wen *et al.*, 2015).

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CaFe_2O_4 has presented good efficiency in photodecomposition application, as well as hydrogen evolution by water splitting. Zhang and Wang (2014) synthesized CaFe_2O_4 by solution combustion method. The as-synthesized material exhibited good photodecomposition efficiency of methylene blue under visible light. Dom *et al.* (2017) reported the good performance of CaFe_2O_4 in hydrogen evolution by water splitting under visible light. Due to its ferromagnetism property, CaFe_2O_4 can be magnetically recovered from water body, when photodecomposition process ends.

Another research interest is the immobilization of photocatalyst onto substrates (Wang *et al.*, 2018). The as-prepared composite has advantages from both components. Many artificial materials have been used as substrates, such as activated carbon or graphene (Mohan and Pittman, 2006; Yang *et al.*, 2018).

Compared with these, natural minerals are considered an alternative option. Among them, diatomite (Dt) has attracted wide attention due to its unique advantages such as hierarchical porous structure, high adsorption ability, high chemical stability, large abundance, and low cost (Wang *et al.*, 2015a). Liu and colleagues reported the immobilization of N-doped TiO_2 onto diatomite by sol-gel method, and the synthesized composite presented an enhanced photocatalytic activity compared with the unsupported one (Chen and Liu, 2016a). This enhancement of photocatalytic activity was attributed to the adsorption ability of diatomite, which attracted the pollutants from water and enriched them around photocatalytic reaction sites, resulting in the improvement of decomposition efficiency.

In this study, diatomite (Dt) was chosen to support magnetic CaFe_2O_4 nanoparticles. Then, we introduced La-doped TiO_2 (La- TiO_2) as the outermost layer of the composite. The photocatalytic efficiency of the ternary composite (La- TiO_2 / CaFe_2O_4 /diatomite, tagged as La-TCD) was evaluated by the decomposition of antibiotic OTC, as well as the disinfection of typical bacteria *Escherichia coli*, in the presence of visible light. From the photodecomposition results, the optimal amount of La dopant, as well as composite dosage, was determined.

Moreover, the interaction between CaFe_2O_4 and La- TiO_2 , as well as the role of substrate diatomite, was illustrated based on the characterization and decomposition results, and the photodecomposition mechanism was proposed. Above all, this work is aimed to the preparation, characterization, and photodecomposition evaluation of ternary La-TCD as photocatalyst for wastewater remediation under visible light or solar light illumination. By combining high adsorption ability, enhanced photodecomposition performance, and simplified reusability, the La-TCD composite could be considered suitable to be applied in wastewater treatment process.

Experimental

Materials

All chemicals used during experimental period were of analytical grade and with no further purification. We purchased crude diatomite from Yuan-Tong Mineral Co. Ltd., and pretreated it by acid leaching method. The obtained sample was used as the substrate of La- TiO_2 / CaFe_2O_4 heterojunction nanoparticles. The pretreatment was carried out based on the literature reported by Liu and colleagues (Chen and Liu, 2016b).

The fabrication of CaFe_2O_4 /Dt powder

The CaFe_2O_4 nanoparticles were dispersed onto substrate diatomite, so as to produce the binary CaFe_2O_4 /Dt composite. The fabrication process was described as follows:

In a typical fabrication process, pretreated diatomite (5.0 g) was mixed with deionized water (20 mL), while ferric nitrate nonahydrate [$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 2.0 g] and calcium nitrate tetrahydrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 0.9 g] were also added into the above mixture, which was then kept under constant stirring. Then citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, 2.5 g) was also added into the above mixture. After 0.5 h, the mixture was heated at 90°C to become dehydrated gel. Then, the gel was calcined at 700°C for 2 h. After annealing and cooling down to room temperature, the obtained product was the CaFe_2O_4 /Dt hybrid powder. Pure CaFe_2O_4 was also prepared based on the above procedure, except for the addition of diatomite.

The fabrication of ternary La-TCD

The fabrication of ternary La-TCD was described as follows: this procedure was aimed at introducing La- TiO_2 as the outermost layer of CaFe_2O_4 /Dt.

In a typical fabrication process, CaFe_2O_4 /Dt (5 g) and acetic acid (10 mL) were added into absolute ethanol (20 mL) and the mixture was kept under constant stirring. After 0.5 h, tetrabutyl orthotitanate (8.0 mL) was added dropwise into the mixture. Another mixture was also prepared: lanthanum nitrate hexahydrate [$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, La precursor, varied amount] was dissolved into the hybrid of deionized water (8.0 mL) and absolute ethanol (24 mL). The obtained mixture was added dropwise into the former one. The as-prepared product was aged for 12 h to turn into gel, and then heated at 90°C and calcined at 450°C for 2 h in a muffle oven, at a heating rate of 5°C/min.

Based on varied amount of lanthanum nitrate hexahydrate, the ternary composite was denoted as La-TCD-1, La-TCD-2, La-TCD-3, and La-TCD-4 [the amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was 0.002, 0.004, 0.01 or 0.02 g].

For comparison, undoped TiO_2 / CaFe_2O_4 /diatomite (TCD) composite was prepared by the above method, except for the addition of La precursor. And unsupported La- TiO_2 / CaFe_2O_4 (La-TC) and La- TiO_2 were also prepared, when the addition amount of La precursor was set as 0.004 g. La- TiO_2 /Dt and TiO_2 /Dt were also prepared to investigate the role of ferrite CaFe_2O_4 .

Characterization

X-ray diffraction (XRD) analysis was performed using model D8-X (Bruke) X-ray diffractometer. Nitrogen adsorption-desorption analysis was performed on catalysts at 77 K to estimate their BET (Brunaure-Emmett-Teller) surface area, using model ASAP-2020 (Micromeritics) physical absorption analyzer. The optical absorption performance of the catalyst was evaluated using model UV-3600 (Shimadzu) diffuse reflectance spectrophotometer. The magnetic properties of the catalysts were characterized using model EV-9 (Hitachi) vibrating sample magnetometer.

Scanning electron microscopy (SEM) analysis was performed using model ULTRA-55 (Carl Zeiss AG) system, and transmission electron microscopy (TEM) measurements were performed using model JEM-2110 system in randomly selected regions under vacuum operating conditions. X-ray

photoelectron spectroscopy (XPS) analysis was performed using model ESCALAB-200 system. The photoluminescence (PL) spectra of catalysts were obtained using model FLS-920 instrument.

Photodecomposition experiments

The photocatalytic activity of all catalyst samples was determined by degrading OTC solution (10 mg/L), carried out under visible light illumination (150 W Xenon lamp, with a filter to screen out UV light). The catalyst sample was mixed with 200 mL of OTC solution under air-equilibrated condition. The reactor was coated with a cooling jacket to keep the mixture's temperature constant. An aliquot of 3 mL was taken every 30 min afterward. The concentration of the solution was estimated using a UV-Vis spectrophotometer (UV3000; Shimadzu). The value of total organic carbon (TOC) was also determined using a TOC analyzer (TOC-500/5050; Shimadzu).

Photo-disinfection experiments

The photo-disinfection activity of all catalyst samples was evaluated by incubating bacterial cells of *E. coli* with every catalyst sample and counting the number of colony-forming units (CFUs). Typically, the bacterial cells were cultured overnight in specific nutrient solution (the aqueous solution of NaCl, tryptone, and yeast extract), and placed under constant shaking in an incubator. The bacteria sample was diluted with NaCl solution, and then mixed with 2.0 g/L of catalyst sample and grown for 180 min at constant temperature of 310 K. The CFU value was set at magnitude of 10^5 CFUs/mL. The photo-disinfection test was illuminated using the illumination source, which was the same Xenon light applied during photodecomposition test.

For comparison, this identical experiment was also carried out under dark condition, so as to explicitly determine the percentage of the photocatalytic decomposition efficiency. During both experiments, aliquots (1 mL) were extracted at separated time intervals (every 30 min) from the mixture and put onto agar plates. The value of CFU was counted and recorded. Similar tests were carried out, when no catalysts were added during the photo-disinfection process. The purpose is to evaluate the effect of light illumination on *E. coli*.

Results and Discussion

Characterization results

The physicochemical properties of catalysts were characterized and analyzed. The results were illustrated and discussed as follows:

The crystalline structures of pure CaFe_2O_4 , $\text{CaFe}_2\text{O}_4/\text{Dt}$, TCD, and various La-TCD samples were compared, and their XRD spectra are shown in Fig. 1. The spectra of pure CaFe_2O_4 and $\text{CaFe}_2\text{O}_4/\text{Dt}$ both showed the typical peaks of spinel-type calcium ferrite (red dots in Fig. 1, JCPDS CARD No. 65-1333) (Zhang and Wang, 2014; Wang *et al.*, 2017). The sharp diffraction peaks as well as high intensity implies the good crystallinity of CaFe_2O_4 . In the XRD pattern of $\text{CaFe}_2\text{O}_4/\text{Dt}$, the intensity of the above peaks decreased. This result might be attributed to the low content of CaFe_2O_4 nanoparticles, which were dispersed onto the surface of diatomite.

Besides, this pattern also presented the typical peaks from diatomite (blue dots in Fig. 1), located at $2\theta = 21.6^\circ$ and

FIG. 1. XRD patterns of pure CaFe_2O_4 , $\text{CaFe}_2\text{O}_4/\text{Dt}$, undoped TC and various La-TCD samples. CaFe_2O_4 , calcium ferrite; Dt, diatomite; La-TCD, lanthanum-doped $\text{TiO}_2/\text{calcium ferrite/diatomite}$; XRD, X-ray diffraction.

26.7° . These two peaks are assigned to the impurities of opal and quartz, respectively (Dong *et al.*, 2018). The main component of diatomite was amorphous silica, and this uncrystalline structure could not be detected by XRD technology. The spectra of ternary TCD and various La-TCD samples also presented the peaks of diatomite.

Moreover, the typical peaks of anatase TiO_2 (JCPDS CARD No. 21-1272) are observed (black dots in Fig. 1), yet the intensities of these peaks seemed slightly decreased after La doping. This result implies that, La doping hindered the crystal growth of TiO_2 particles. The introduction of La dopant

FIG. 2. The BET isotherms and specific surface area values of undoped TCD and La-TCD-2. BET, Brunauer-Emmett-Teller.

led to the formation of La-O-Ti bond on the surface as well as the interstitial site of TiO_2 lattice, thus inhibiting the crystal growth of TiO_2 during calcination period (Wei *et al.*, 2004).

The surface condition of catalyst has been considered one of the most critical factors of its photocatalytic activity (Xia *et al.*, 2014). In this work, the N_2 adsorption-desorption isotherms of undoped TCD and La-TCD-2 were compared. As indicated in Fig. 2, both isotherms are classified as type IV based on Brunauer S., Deming L. S., Deming W. E. and Tell E. (BDDT) classification, with H3-type hysteresis loops, presenting its typical mesoporous surface condition (Xia *et al.*, 2014).

The BET-specific surface area of TCD and La-TCD-2 is estimated to be 50.7 and 58.0 m^2/g , respectively. The slightly increased surface area value is ascribed to the introduction of La dopant. The hindering effect of La doping toward the crystal growth of TiO_2 resulted in smaller crystal size of TiO_2 grain, which improved its surface condition (Wei *et al.*, 2004). The relatively larger specific surface area and mesoporous structure are considered the guarantee of adsorption ability and rapid diffusion of target pollutant molecules, greatly enhancing the photodecomposition performance.

The morphology of La-TCD-2 sample was studied by both SEM and TEM methods.

Figure 3a and b present the SEM images of the sample. The typical disk topography of diatom is clearly observed, including the mesoporous structure. The fragments on the surface of diatom shell might originate from smaller diatom cells or the collapse of other diatom shells. This typical porous structure has been reported beneficial to its adsorption ability (Wang *et al.*, 2015b). The roughness of diatom shell implies that both TiO_2 and CaFe_2O_4 particles were well dispersed onto its surface. This is further proved by the TEM

images of La-TCD-2 (Fig. 3c, d), from which we noticed the hybrid structure of the sample, where La-TiO_2 and CaFe_2O_4 nanoparticles were evenly deposited on the surface of diatom shell.

Furthermore, the supported nanoparticles presented different color, where a number of La-TiO_2 particles were in light color and located at the outermost part, and many inner adjacent CaFe_2O_4 particles were in dark color. The intense interaction between both components enhanced the capability of charge transfer as well as mass migration, resulting in the improvement of photodecomposition performance.

XPS method was applied to La-TCD-2 sample to investigate its surface chemical states and electronic states of surface elements. The XPS results are shown in Fig. 4.

Figure 4a presents the survey spectrum of La-TCD-2, including O, Ti, Si, La, Fe, Sr, and C elements. This result fully validates the existence of composition elements from three components. Among these, carbon element is ascribed to the exogenous carbon contaminant originated from XPS analytical instrument or external environment.

Figure 4b shows the spectrum of Ti ion, and its two peaks that located at 464.3 and 458.4 eV are attributed to $\text{Ti } 2p_{1/2}$ and $\text{Ti } 2p_{3/2}$, respectively. This result implies that Ti exists as Ti^{4+} from anatase-phase TiO_2 (Tian *et al.*, 2016).

Figure 4c shows the Ca 2p XPS spectrum. Two typical peaks of Ca ion with binding energy values of 346.8 and 350.8 eV are in agreement with $\text{Ca } 2p_{3/2}$ and $\text{Ca } 2p_{1/2}$ (Police *et al.*, 2014; Liu *et al.*, 2017). Figure 4c shows the XPS spectrum of Fe ion. The peaks of Fe ion spectrum that locate at 725.9 and 712.4 eV are ascribed to $\text{Fe } 2p_{1/2}$ and $\text{Fe } 2p_{3/2}$, meaning that Fe exists as Fe^{3+} (Vijayaraghavan *et al.*, 2016). The results from Fig. 4c and d prove the existence of CaFe_2O_4 .

FIG. 3. (a, b) SEM images of La-TCD-2; (c, d) TEM images of La-TCD-2. SEM, scanning electron microscopy; TEM, transmission electron microscopy.

FIG. 4. XPS spectra of La-TCD-2: (a) survey spectrum; (b) Ti 2p spectrum; (c) Ca 2p spectrum; (d) Fe 2p spectrum; (e) O 1s spectrum; (f) La 3d spectrum. XPS, X-ray photoelectron spectroscopy.

The XPS peak of O 1s is shown in Fig. 4e. The deconvolution result of O 1s spectrum provides two characteristic peaks. The peak at ca. 530.1 eV is attributed to the oxygen from hydroxyl group (Sun *et al.*, 2018). The other peak at ca. 532.4 eV is ascribed to the presence of oxygen from Si-O-Fe or Fe-O-Ti (Sun *et al.*, 2017). This result suggests that the electron moved between Fe (from CaFe_2O_4) and Si (from diatomite), or between Fe (from CaFe_2O_4) and Ti (from TiO_2) through the intermediate O atom, which results in the formation of Si-O-Fe or Fe-O-Ti bonds (Police *et al.*, 2014). This bonding feature facilitates the interface interaction, enhancing charge transfer ability.

Figure 4f shows the La 3d spectrum of La-TCD-2. Its two peaks that locate at 835.1 and 851.9 eV are attributed to La $3d_{5/2}$ and La $3d_{3/2}$, respectively. These binding energy values imply the formation of La-O-Ti bonds, compared with the values of La ion from La_2O_3 (Zhou *et al.*, 2016). The formation of La-O-Ti bonds introduces impurity band to the bandgap of TiO_2 lattice.

Figure 5 presents the UV-vis light absorption spectra of $\text{CaFe}_2\text{O}_4/\text{Dt}$, $\text{La-TiO}_2/\text{Dt}$, and La-TCD-2.

The binary $\text{CaFe}_2\text{O}_4/\text{Dt}$ showed intense absorption in both UV region and visible light region, with the absorption edge at ca. 710 nm, corresponding to the bandgap of CaFe_2O_4 as 1.85 eV (Police *et al.*, 2014; Zhang and Wang, 2014). $\text{La-TiO}_2/\text{Dt}$ showed strong absorption signal in UV region, which is attributed to component TiO_2 . Its absorption edge was at ca. 440 nm, implying the effect of La doping, which extended the light absorption of TiO_2 by narrowing its

bandgap (the absorption edge of pristine TiO_2 is 387 nm). The ternary La-TCD-2 showed similar absorption intensity in visible light region, due to the component CaFe_2O_4 .

Also, its higher light absorption intensity below 440 nm is attributed to the component TiO_2 . The improved light absorption capability of La-TCD-2 can basically be ascribed to the components La-TiO_2 and CaFe_2O_4 . The ternary sample showed higher light absorption than binary $\text{La-TiO}_2/\text{Dt}$, implying its possibility of an improved photocatalytic activity.

FIG. 5. DRS absorbance spectra of $\text{La-TiO}_2/\text{Dt}$, $\text{CaFe}_2\text{O}_4/\text{Dt}$, and La-TCD-2. La-TiO₂, La-doped TiO₂.

The magnetic properties of $\text{CaFe}_2\text{O}_4/\text{Dt}$ and La-TCD-2 were measured by Vibrating Sample Magnetometer (VSM) method, and the results are indicated by plotting saturation magnetization (M) against coercivity (H_c), shown in Supplementary Fig. S1a. Both plots indicate the magnetic hysteresis loops of $\text{CaFe}_2\text{O}_4/\text{Dt}$ and La-TCD-2 at room temperature. The magnetic saturation (M) values of $\text{CaFe}_2\text{O}_4/\text{Dt}$ and La-TCD-2 were measured to be 2.59 and 1.29 emu/g. The difference value might be ascribed to the introduction of nonmagnetic La-TiO_2 nanoparticles, which were located at the outermost layer and reduced the ferromagnetism of the composite, resulting in the decrease of M value.

However, despite the decrease of magnetism compared to $\text{CaFe}_2\text{O}_4/\text{Dt}$, the ternary La-TCD-2 composite can be efficiently separated from OTC solution by an external magnet (Supplementary Fig. S1b).

Photodecomposition performance

The performance of different catalysts. The photoactivity of La-TCD sample was studied by the decomposition of OTC under visible light, while undoped TCD, unsupported $\text{La-TiO}_2/\text{CaFe}_2\text{O}_4$ (La-TC), $\text{CaFe}_2\text{O}_4/\text{Dt}$, $\text{La-TiO}_2/\text{Dt}$, La-TiO_2 , and TiO_2/Dt were also applied as comparison. The results are shown in Fig. 6b. The dosage of each catalyst was fixed as 2.0 g/L (the ratio of solid phase to liquid phase). The adsorption toward OTC under dark environment was also

studied and is presented in Fig. 6a. It is concluded that under dark condition, the adsorption-desorption equilibrium of the suspension was achieved after 30 min. Based on the result, we first launched 30 min of dark period before the visible-light-driven decomposition experiment.

The result presented in Fig. 6b implies that, among all catalyst samples, La-TCD showed highest photoactivity. This result can be clearly presented by the value of reaction rate constant calculated by the following equation:

$$\ln\left(\frac{C_t}{C_i}\right) = kt \quad (1)$$

where k represents the reaction rate constant, t represents the illumination time, C_i represents the concentration of OTC solution when light illumination was initiated, and C_t represents the concentration of OTC solution at the illumination time (t). It has been reported that, this photodecomposition reaction constant is independent of pollutant concentration or temperature, since the photodecomposition process only depends on the illumination flux and spectrum of the light source (Wang *et al.*, 2015b). The fitted kinetic plots are presented in Fig. 6c, and the rate constants are shown in Supplementary Table S1.

Figure 6b and c imply that TiO_2/Dt showed no photoactivity under visible light. Pristine TiO_2 only presents photoactivity under UV light, although it was immobilized onto

FIG. 6. The removal rate of OTC: (a) under dark condition for 90 min; (b) using different catalyst samples under visible light illumination; (c) the corresponding kinetic plots; (d) the TOC removal ratio. OTC, oxytetracycline; TOC, total organic carbon.

diatomite. After the introduction of La dopant, La-TiO₂/Dt showed obvious visible-light-driven photoactivity. A similar result was observed when we compared the photoactivity between La-TCD and undoped TCD, that is, the former one showed higher photoactivity. La doping led to the formation of new impurity level below the conduction band (CB) of TiO₂, which narrowed the bandgap of TiO₂ and extended its light absorption (reflected by the results of UV-vis diffuse reflectance Spectrum).

Moreover, La dopant plays a role as electron acceptor, hindering the recombination of photo-induced charge carriers and resulting in the enhancement of photoactivity (Zhou *et al.*, 2016). The higher surface area was beneficial to the adsorption ability and photodecomposition efficiency.

Among all La-TCD samples, La-TCD-2 showed highest photoactivity, meaning that this catalyst represented the optimal amount of La dopant. The introduction of excessive La dopant led to the decrease of photoactivity, which might be related to its role during photocatalytic process. When the doping amount of La in TiO₂ surpasses a certain limit, La cation changes its role from electron acceptor to recombination center for photo-induced charge carriers, reducing the photoactivity of La-TCD (Wei *et al.*, 2004; Zhou *et al.*, 2016).

Ternary La-TCD-2 showed better photodecomposition performance than La-TiO₂/Dt, implying that the interaction between La-TiO₂ and CaFe₂O₄ might enhance the photoactivity of La-TCD. The sample La-TCD-2 showed higher photoactivity than unsupported La-TC sample, which is ascribed to substrate diatomite. A similar result is noticed when we compare the photoactivity between La-TiO₂/Dt and La-TiO₂. As an excellent adsorbent, diatomite was capable of capturing OTC molecules from the solution phase, thus increasing the quantity of OTC molecule around TiO₂ particles, which was beneficial to the decomposition reaction (Wang *et al.*, 2015a; Sun *et al.*, 2018).

The mineralization of OTC was indicated by the TOC removal ratio at different time intervals. The result is shown in Fig. 6d. As can be seen, this TOC result accords with the above photodecomposition result of OTC, that is, the ternary La-TCD-2 catalyst showed highest removal efficiency under visible light.

The effect of catalyst dosage. Different dosages of ternary La-TCD-2 sample were applied in the photodecomposition experiment, to determine the effect of catalyst dosage. The dosage was set as follows: 1.0, 2.0, 3.0, and 5.0 g/L. The decomposition results are shown in Supplementary Fig. S2a, the corresponding kinetic plots are shown in Supplementary Fig. S2b, and the rate constants are presented in Supplementary Table S2.

We noticed that, the optimal solid/liquid ratio was 2.0 g/L, implying that excessive amount of catalyst resulted in reduced decomposition rate. This might be ascribed to the light shielding effect (Chen and Liu, 2017b; Chen *et al.*, 2019a, 2019b); in other words, when extra amount of catalyst was added into OTC solution, less light reaches the surface of the catalyst, since the surrounding ones give their shade onto the surface. Finally, lowered exposure area results in reduced photoactivity (Wu and Zhang, 2019a, 2019b).

The effect of pH. OTC residue has been detected in various types of water bodies with varied pH values. Thus, the effect of initial pH value on photodecomposition performance was also studied.

The initial pH value of OTC solution was varied using HCl or NaOH, to evaluate its effect on OTC photodecomposition performance. La-TCD-2 was used as catalyst.

As shown in Supplementary Fig. S3, when pH value was 6, the removal rate of OTC was 97.0%, meaning that this condition showed the lowest hindering effect.

The effect of pH value could be attributed to the structure of OTC and the surface condition of La-TCD-2.

First, the main component of La-TCD-2 is diatomite; thus, the pH value might have an effect on its surface charge, since its isoelectric point (IEP) is ca. 5 (Liu *et al.*, 2012). Thus, the surface charge of diatomite would become positive if pH < 5, due to the formation of SiOH₂⁺, and its surface charge would become negative if pH > 5, along with the formation of SiO⁻. Moreover, the amount of its surface charge could be altered by pH value, which in turn affected its adsorption ability (Chao *et al.*, 2014).

Second, as shown in Supplementary Fig. S4, OTC molecule is basically composed of tricarbonyl group, phenolic diketone group, and dimethylammonium group, whose pKa values are 3.3, 7.5, and 8.9, respectively (Figuerola *et al.*, 2004; Sassman and Lee, 2005). So when pH < 3.3, OTC was protonated as H₃OTC⁺. When pH value was between 3.3 and 7.5, OTC became zwitterions form (H₂OTC[±]), due to the loss of hydrogen. When pH > 7.5, OTC turned into HOTC⁻ and OTC₂⁻. Above all, we deduced that, when pH < 3.3, the positively charged surface of diatomite might repulse H₃OTC⁺, which weakened the adsorption capability of La-TCD-2, vice versa, when pH value was between 7.5 and 8.9, the negatively charged surface of diatomite might repulse HOTC⁻ and OTC₂⁻, the adsorption capability of La-TCD-2 could also be weakened.

Third, as the outermost layer of La-TCD-2, the IEP of TiO₂ is ca. 6.3 (Luo *et al.*, 2010), that is, the surface of TiO₂ could be positively charged if pH < 6.3, which might make the photo-generated electrons move to its surface and combine with O₂ to generate •O₂⁻, which was one of the active species during photodecomposition process. When pH > 6.3, the surface of TiO₂ could be negatively charged, which resulted in the immigration of photo-generated holes to its surface, and then these holes reacted with H₂O to form •OH, which was another active species during photodecomposition process. However, if the pH value was much higher or lower than IEP, the formation of those active species could be suppressed (Zhao *et al.*, 2013).

The active species during OTC photodecomposition. The photodecomposition process was basically ascribed to the formation of photo-induced charge carriers. Then these charge carriers interact with nearby OH⁻ ions or O₂ molecules dissolved in water and form superoxide ions (•O₂⁻) and hydroxyl radicals (•OH), which then participated in the decomposition process, along with photo-induced holes (Xue *et al.*, 2019). The effects of those active species generated from La-TCD catalyst were evaluated by scavengers, such as ammonium oxalate (AO, h⁺ scavenger, 10 mmol/L), isopropanol (IPA, •OH scavenger, 10 mmol/L), or benzoquinone (BQ, •O₂⁻ scavenger, 0.2 mmol/L), and the results are presented in Supplementary Fig. S5.

These results indicate that IPA presented highest inhibiting effect. This probably proved that •OH played a crucial role compared with others during the photodecomposition process. It is reported that, hydroxyl group (•OH) plays a

crucial role during photodecomposition process, cleaving carbon rings of OTC molecule, which results in the collapse of OTC into smaller molecules (Qiang *et al.*, 2018).

The photodisinfection performance of La-TCD. The visible-light-driven disinfection activity of La-TCD catalyst sample was also evaluated against bacteria *E. coli* (Fig. 7b). The effect of light illumination was also evaluated, when no La-TCD catalysts were added during the test (Supplementary Fig. S6); the result indicated that *E. coli* viability was not influenced by visible light illumination.

No significant decrease of cell viability of *E. coli* was observed under 2 h of dark condition, and this result indicates that the selected bacteria survived in dark environment. However, 94.0% decrease in cell viability of the bacteria was observed after 2 h of visible light illumination when the sample La-TCD-2 was applied (Fig. 7a, and the disinfection percentages after 2 h under dark or under visible light illumination are compared and presented in Supplementary Fig. S7).

La-TCD-2 showed the best disinfection efficiency compared with other catalyst samples. The above results imply that the ternary La-TCD presented strong photocatalytic disinfection activity toward selected bacteria, meaning that La-TCD was capable of killing bacteria *E. coli* under visible light.

The scavenging tests were also performed to determine how effective those reactive species were during this photodisinfection reaction (Supplementary Fig. S8). We also carried out similar tests without La-TCD catalysts, to evaluate the single effect of scavenger on bacteria viability (Supplementary Fig. S9). The results indicate that scavenger alone did not affect the viability of *E. coli* under visible light.

Supplementary Figure S8 implies that photo-induced holes showed little hindering effect during disinfection test, according to the plot of AO (10 mmol/L). However, when IPA (10 mmol/L) or BQ (0.2 mmol/L) was added as scavenger, the cell viability was highly increased, compared with the test without any scavenger. The order of the scavenging followed

this sequence: IPA > BQ > AO. Apparently, the increase of cell viability in the presence of IPA or BQ confirmed that the photodisinfection was mainly initiated by $\cdot\text{OH}$ and $\cdot\text{O}_2^-$ radicals. From photocatalytic disinfection performance, it can be concluded that La-TCD can be used as a potential photocatalytic disinfection agent against waterborne bacteria.

The reusability of La-TCD. The reusability of ternary La-TCD-2 was evaluated, and Supplementary Figs. S10 and S11 reflect the recycling performance of La-TCD during OTC photodecomposition process and *E. coli* photodisinfection process. After one turn of repetition test, catalyst sample was collected by an external magnet and washed by deionized water and ethanol thrice. Then it was dried at 80°C for the next turn. After five repetition tests, the removal rate of OTC remained 89.6%, compared with 92.0% at first use; similarly, after five turns, the survival percentage of *E. coli* was 17.1%, compared with 13.1% at first use, suggesting that La-TCD exhibited good stability and reusability during both photodecomposition and photodisinfection processes.

Photodecomposition mechanism

Based on the above contents, La doping introduced impurity band below the CB of TiO_2 , meanwhile acting as electron acceptor to hinder the recombination of charge carriers. The introduction of La dopant improved the visible-light-driven catalytic activity of TiO_2 .

Thus, we proposed the possible mechanism of La-TCD based on the above contents (illustrated in Fig. 8).

First, the OTC molecules were adsorbed onto the surface of La-TCD due to the strong adsorption ability of substrate diatomite (Li *et al.*, 2015; Wang *et al.*, 2015a).

Second, due to the introduction of La dopant, the narrowed bandgap of TiO_2 enabled the electron (e^-) to be stimulated to the impurity level of TiO_2 under visible light illumination, leaving hole (h^+) in the VB (valence band) of TiO_2 . The electron would then be further stimulated to the CB of TiO_2 . Meanwhile, due to the narrow bandgap value of CaFe_2O_4 , its electron was excited by visible light illumination, which

FIG. 7. (a) The photodisinfection result of *Escherichia coli* using catalyst samples under visible light illumination; (b) the disinfection results of *E. coli* under dark condition.

FIG. 8. Proposed mechanism for OTC photodecomposition reaction using La-TCD-2.

ended up with the generation of electrons (on the CB) and holes (on the VB).

Third, since the CB potential of CaFe_2O_4 is higher compared with TiO_2 , and the VB potential of TiO_2 is lower compared with CaFe_2O_4 , electron transfer is expected from the CB of CaFe_2O_4 to CB of TiO_2 . Similarly, the holes on the VB of TiO_2 migrated to the VB of CaFe_2O_4 . The above charge carriers moved across the interface of the heterostructure, and this movement facilitated the separation of photo-generated electron-hole pairs, hindering their recombination process, meaning that more charge carriers were captured by O_2 or OH^- to form $\cdot\text{O}_2^-$ or $\cdot\text{OH}$, which ended up with the enhancement of photodecomposition efficiency (Police *et al.*, 2014).

The proposed mechanism was further proved by the results of PL characterization, which reflected the recombination

intensity of photo-generated electron-hole pairs. The PL spectra of $\text{CaFe}_2\text{O}_4/\text{Dt}$, undoped TCD, and La-TCD-2 are shown in Fig. 9a.

From the spectra, the peak located at 400–500 nm is attributed to the charge carrier transition (Wang *et al.*, 2015b). The intensity order of three PL spectra is as follows: $\text{CaFe}_2\text{O}_4/\text{Dt} > \text{TCD} > \text{La-TCD-2}$, meaning that, the interaction between TiO_2 and CaFe_2O_4 quenched the PL intensity of the catalyst. Due to the charge transfer process, which took place at the interface between CaFe_2O_4 and La- TiO_2 , the charge recombination on the surface of TiO_2 was suppressed, resulting in the decrease of PL intensity. A similar result was observed when we compared the PL intensity values of TCD and La-TCD-2. This is ascribed to the introduction of La dopant, which acts as electron acceptor and hindered the

FIG. 9. (a) The photoluminescence spectra and (b) time-resolved fluorescence spectra of $\text{CaFe}_2\text{O}_4/\text{Dt}$, undoped TCD and La-TCD-2.

recombination of photo-induced charge carriers, thus promoting the photocatalytic activity of the catalyst.

To better understand the mobility of photo-generated electron-hole pairs, the time-resolved fluorescence spectra of three catalysts were recorded (shown in Fig. 9b). The average lifetimes of electron-hole pairs are 5.21, 6.24, and 7.41 ns for $\text{CaFe}_2\text{O}_4/\text{Dt}$, TCD, and La-TCD-2, respectively. This result implies that the heterojunction between CaFe_2O_4 and TiO_2 helped prolong the photo-induced charge lifetime.

Conclusion

In this work, magnetically recyclable La-doped TiO_2 /calcium ferrite/diatomite (La-TCD) composite was successfully fabricated by sol-gel method, and its photocatalytic activity was investigated by the decomposition of OTC and disinfection of *E. coli* under visible light. Based on the experimental results, optimal amount of La dopant was determined (La-TCD-2), as well as the catalyst dosage (the optimal solid/liquid ratio was 2.0 g/L).

La-TCD presented better performance than La- TiO_2 / CaFe_2O_4 or $\text{CaFe}_2\text{O}_4/\text{Dt}$. The carrier diatomite promoted the decomposition efficiency by adsorbing OTC molecules onto the surface of La-TCD. The introduction of La dopant, as well as the charge transfer between TiO_2 and CaFe_2O_4 further improved the visible-light-driven photocatalytic activity. La-TCD presented good reusability after five cycles, suggesting itself promising for treating waterborne bacteria and organic pollutants.

Author Disclosure Statement

No competing financial interests exist.

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Supplementary Material

Supplementary Figure S1
Supplementary Figure S2
Supplementary Figure S3
Supplementary Figure S4
Supplementary Figure S5
Supplementary Figure S6
Supplementary Figure S7
Supplementary Figure S8
Supplementary Figure S9
Supplementary Figure S10
Supplementary Figure S11
Supplementary Table S1
Supplementary Table S2

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