

铁、铈共掺杂纳米 TiO₂ 溶胶的制备及抗菌性能

王 虹¹ 王 鹏^{*,1,2}

(¹ 城市水资源与水环境国家重点实验室, 哈尔滨工业大学, 哈尔滨 150090)

(² 哈尔滨工业大学市政环境工程学院, 哈尔滨 150090)

摘要: 采用微波辅助胶溶工艺, 在常压条件下, 制备了可用于室内杀菌的铁、铈共掺杂纳米 TiO₂ 水溶胶, 通过 X-射线衍射(XRD)、等离子体发射光谱(ICP)、动态光散射(DLS)、透射电镜(TEM)和 X 射线光电子能谱(XPS)对产物结构进行了表征, 并选用白色葡萄球菌、大肠杆菌和枯草芽孢杆菌为受试菌种, 分别在无光照、自然光照条件下, 采用菌落计数法对水溶胶抗菌性能进行了检测。结果表明, 用微波辅助胶溶工艺制备的 Fe/Ce 共掺杂纳米 TiO₂ 为锐钛矿型, 其平均粒径为 10 nm。Fe/Ce 的掺杂改性能有效提高纳米 TiO₂ 水溶胶的抗菌性能, 尤其是在自然光照条件下, Fe/Ce 共掺杂纳米 TiO₂ 溶胶在 6 h 内对各测试菌种的杀菌率均为 95%以上, 表明 Fe/Ce 共掺杂纳米 TiO₂ 水溶胶具有很高的广谱杀菌性。采用透射电镜(TEM)对杀菌过程中的大肠杆菌菌体形态进行观测, 探讨了 Fe/Ce 共掺杂纳米 TiO₂ 水溶胶的抗菌机理。

关键词: 微波辅助胶溶; Fe/Ce 共掺杂; TiO₂ 溶胶; 抗菌性能; 机理

中图分类号: O648.16 文献标识码: A 文章编号: 1001-4861(2009)11-1928-07

Preparation and Antibacterial Property of Fe/Ce Codoped Nano-Titanic Hydrosol

WANG Hong¹ WANG Peng^{*,1,2}

(¹State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090)

(²School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090)

Abstract: The Fe/Ce codoped nanometer titanic hydrosol, which could be applied to indoor antiseptis, was prepared under atmospheric pressure by microwave-assisted peptization process. The products were characterized by X-ray diffraction (XRD), inductively coupled plasma-atomic emission spectrometry (ICP), dynamic light scattering(DLS), transmission electron microscope(TEM), and X-ray photoelectron spectrometer(XPS). Using colony counting experiment to make sure the hydrosol had good antibacterial performance. The results showed that these Fe/Ce codoped nano TiO₂ hydrosol particles prepared by microwave-assisted peptization process without calcinations treatment had anatase crystal structure, and the average size was 10.8nm. The result of antibacterial experiment showed the Fe/Ce codoped nano-TiO₂ hydrosol had better antibacterial performance than the pure nano-TiO₂ hydrosol. The relative antibacterial rate exceeded 95% when the illumination of natural light irradiation lasted for 6 h, and there was no discrepancy for different strains. So Fe/Ce codoped nano-TiO₂ hydrosol has a potent and broad spectrum antibacterial performance. The morphological change of Escherichia coli were observed by transmission electron microscope(TEM), and the antibacterial mechanism of Fe/Ce codoped nano-TiO₂ hydrosol was discussed.

Key words: microwave-assisted peptization; Fe/Ce codoped; TiO₂ hydrosol; antibacterial property; mechanism

收稿日期: 2009-07-28。收修改稿日期: 2009-09-16。

国家自然科学基金资助项目(No.50678045)。

*通讯联系人。E-mail: pwang73@vip.sina.com

第一作者: 王 虹, 女, 31 岁, 博士研究生; 研究方向: 微波辅助制备纳米二氧化钛水溶胶。

Titanium dioxide is broadly used as a photocatalyst^[1~5], such as in wastewater treatment, because it is photochemically stable, non-toxic and cost little^[6~8].

The nano-TiO₂ hydrosol is a new product in nanometer titanium oxide field, which can be applied to indoor organic degradation and antiseptics^[9,10]. The particles in TiO₂ hydrosol are anatase crystal structure. The TiO₂ sol has uniform distribution and better dispersion in water, and has stronger interfacial adsorption ability^[11~15]. It can easily coat on different supporting materials like polymers, optical fibres, wood and plastics.

It can be prepared by the chemical coprecipitation-peptization method^[16,17]. The microwave-assisted peptization process had been researched in prior work. (CN101157477).

To further increase of the photocatalytic and antibacterial activities of TiO₂, many studies have succeeded to put ferrum iron oxides into TiO₂ structure via high temperature treatment to eliminate the recombination of holes(h⁺) and electrons(e⁻)^[18~25]. And rare-earth elements doped TiO₂ are also a research focus^[26~28]. However, the effect of Fe/Ce co-doped to TiO₂ sol particles structure and antibacterial activity, at low-temperature condition under microwave irradiation, had not been extensively investigated so far.

In this study, Fe/Ce-TiO₂ sol was prepared using the coprecipitation-peptization under microwave irradiation. The antibacterial activity of this sol sample was evaluated by bacteriostatic experiments under natural light. And the antibacterial mechanism was discussed basically.

1 Experimental

1.1 Preparation of Fe/Ce-TiO₂ hydrosol by Microwave-assisted peptization under atmospheric pressure

Anhydrous ferric chloride(FeCl₃) and ammonium cerium(IV) nitrate(Ce(NH₄)₂(NO₃)₆) was dissolved in 12.5 cm³ concentrated hydrochloric acid aqueous solution according to the required doping content(Fe³⁺ dopant equivalent to 0.05at% of Ti⁴⁺ and Ce⁴⁺ dopant equivalent to 0.1 at% of Ti⁴⁺). TiCl₄ solution (3.3 cm³) was dripped into the above acidic solution then vigorously

stirred for 1 h. In order to ensure the hydrolysis reaction went to completion, 10wt% NH₃·H₂O aqueous solution was added dropwise into TiCl₄ solution to obtain a precipitate, giving an ultimate colloid with pH value of 8. To remove residual NH₄⁺ and Cl⁻ ions, the precipitate was adequately washed with deionized water and vacuum-filtered until Clions couldnt be determined using silver chloride(AgCl) solution(0.1 mol·L⁻¹). Then, the acquired precipitate was well dispersed into water and stirred at room temperature for 2 h, meanwhile adding definite nitric acid as peptization catalyst and phasetransfer accelerant. Finally, the above suspension (rough TiO₂ sol) was peptized for 40 min at 80 °C under atmospheric pressure by microwave irradiation, and the 0.05at% ferric ion and 0.1at% cerium ion co-modified TiO₂ sol was formed, having uniform, stable, and transparent properties (Fe/Ce-TiO₂ sol). The pure TiO₂ sol was prepared with the same procedure, omitting the ion dopant. Fe/Ce-TiO₂ or pure TiO₂ powder was prepared from the corresponding sol sample through drying at 40 °C for 24 h.

1.2 Characterization

XRD analysis of samples was carried out on an X-ray diffractometer(XRD-6000, Shimadzu, Japan) under the following conditions: graphite monochromatic copper radiation(Cu Kα, λ=0.154 18 nm); 50 kV as accelerating voltage; 40 mA as emission current; and the 2θ range of 10°~90°.

To validate the amounts of the elements doped in TiO₂ hydrosol, the inductively coupled plasma-atomic emission spectrometry(ICP) was applied.

To study the particulate size of catalysts in hydrosol, light scattering size analysis was carried out using a Malvern 3000 HSA Zetasizer (Malvern Instruments, UK).

The shape and the particulate size of catalysts were observed by transmission electron microscope (TEM).

The surface compositions and chemical states of the samples were examined by a PHI5700X X-ray photoelectron spectrometer(Physics Electron Inc, USA) using a monochromatic aluminium X-ray source. All binding energies (BE) were calibrated by the BE(284.6

eV) of C1s, which gave BE values within an accuracy of ± 0.1 eV.

1.3 Evaluation of the antibacterial activity of Fe/Ce-TiO₂ sol

According to the application of the hydrosol, the sample tiles were prepared. 0.2 mL Fe/Ce-TiO₂ sol or pure TiO₂ sol samples with certain concentration were coated on the surfaces of cleaned tiles (38×75 mm²). Then the tiles were dried at 40 °C for 24 h. Then the sample tiles and the blank tiles were sterilized for 20 min by UV bactericidal lamp in the superclean bench, and placed into culture plates to reserve for the follow experiments.

A bacterial suspension of *Escherichia coli* (*E.coli*), *Bacillus subtilis* (*B.subtilis*) or *Staphylococcus albus* (*S. albus*) was diluted to 10^3 cuf·mL⁻¹ (cuf=colony forming units). 0.1 mL three bacterial suspensions were doped on the surfaces of Fe/Ce-TiO₂ film, pure TiO₂ film, P25 film and blank tile, respectively. The natural light irradiation was lasted for 0.5, 1, 2, 4 and 6 h. The nutrient agar media were injected into the culture plates at the corresponding action time. The agar plates were then inverted and incubated at 37 °C for 12 h. The number of colonies was counted to calculate the antibacterial activity.

To understand the actual antibacterial effectiveness of Fe/Ce-TiO₂ sol in application of indoor antiseptis, the experiments were proceed under analogous indoor environment. The sample tiles and blank tiles, which had been sterilized, were placed in a warm and dankish room for some time under dark and natural light irradiation, respectively. The nutrient agar media were injected into the culture plates at the corresponding action time. The agar plates were then inverted and incubated at 37 °C for 12 h. The number of colonies was counted to calculate the antibacterial activity.

All tests were repeated three times and average data were taken as the final results.

1.4 Discussion of the antibacterial mechanism of Fe/Ce-TiO₂ sol

The changes of apparent shape and structure of *E. coli* during variant phases were observed by transmission electron microscope(TEM).

2 Results and discussion

2.1 Crystal structure

The phase characteristics of TiO₂ and Fe/Ce-TiO₂ particles were investigated by X-ray diffraction. Fig.1 showed that rough TiO₂ sol particles showed mainly scattered peaks, which means it still had a predominantly amorphous structure. Although some either nearly linear or branched oligomers(-Ti-O-Ti-O-) could be formed through the hydrolysis, precipitation, and neutralization pretreatment from the precursor of TiCl₄, Ti(OH)₄ and TiO(OH)₂, it did not complete the condensation-polymerization process. Therefore, it still could not form a regular long-range order of composition atoms arrangement within the bulk phase of rough TiO₂ particles. It can also be seen that the pure TiO₂ sol sample had showed an anatase crystal structure due to diffraction peaks at $2\theta=25.3^\circ, 37.7^\circ, 47.7^\circ, 54.3^\circ, 63.2^\circ$ and 68.9° , which indicates that TiO₂ sol had gradually transformed into a regular anatase crystal structure after peptization-aging treatment under microwave irradiation.

Fe/Ce-TiO₂ sol showed the presence of peaks at $2\theta=25.3^\circ, 37.7^\circ, 47.6^\circ, 54.2^\circ$ and 63.2° , which was regarded as an indicator of anatase, and no other new crystal phase appeared apart from the anatase phase. It can be seen from Fig.1 that there are no reflections o-

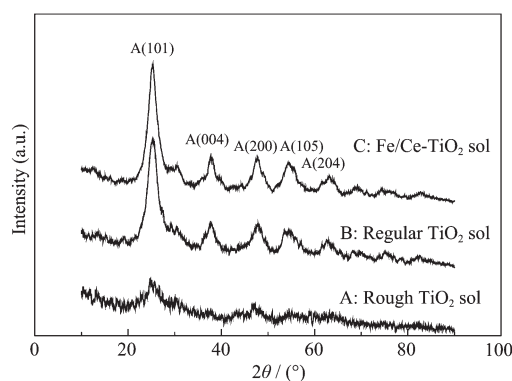


Fig.1 XRD patterns of Fe/Ce-TiO₂ sol, TiO₂ sol and rough TiO₂ sol particles

Table 1 Results of the quantitative elementary analysis

Sample	Contents of element / (mg·kg ⁻¹)		
	Ti	Fe	Ce
Fe/Ce-TiO ₂	1.179×10^3	0.682	3.268

reginating ferrum iron oxides or cerium oxides. A possible reason was that the amount of ferrum iron and cerium ions were too low to be detected by XRD due to the limit of precision of the apparatus.

2.2 ICP analysis

The component analyses of the dopant ions in Fe/Ce- TiO_2 were determined by ICP.

The relative contents of Fe and Ce to Ti were 0.05at% and 0.1at% respectively, they were in consistency with theoretic calculations.

2.3 Particle size distribution

The particle size distribution of TiO_2 catalysts greatly influences their properties of adsorption and antibacterial activity. In this study, the particle size of TiO_2 and Fe/Ce- TiO_2 sol was analyzed by the light-scattering size analyzer, and the particle size distribution of different catalysts is presented in Fig.2. The results demonstrate that the pure TiO_2 sol had a particle size distribution in the range 4.9~30.7 nm with a mean value of 10 nm and Fe/Ce- TiO_2 sol had an average size of 10.8 nm and particle size distribution from 6.2 to 30.9 nm. These data confirmed that both the TiO_2 sol and Fe/Ce- TiO_2 sol had a uniform particle size distribution, which can make the hydrosol catalytic stabilized. Furthermore, the average size of Fe/Ce- TiO_2 sol is a little bigger than the pure TiO_2 sol particles. Integrating with the below results of XPS, the reason is that the modification by ferric and cerium ions would be beneficial to adsorption properties of the sol particles to hydroxyl groups and water molecules, which leads to the hydrated layer of Fe/Ce- TiO_2 sol particle was thicker than that of TiO_2 sol particle in hydrosol.

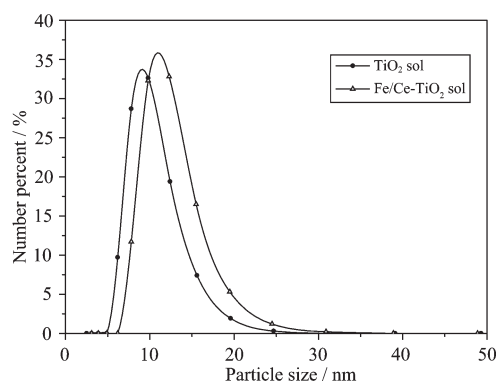


Fig.2 DLS spectra of TiO_2 sol and Fe/Ce- TiO_2 sol

2.4 TEM analysis

The shape and the particulate size of TiO_2 and Fe/Ce- TiO_2 particles observed by TEM. In the Fig.3 and Fig.4, both the pure TiO_2 nanoparticles and the Fe/Ce- TiO_2 nanoparticles were all spherical. Their particle size distributions and average sizes were coincident with the foregoing corresponding DLS results respectively. It was confirmed once again that the Fe/Ce codoping had no negative effect on the particle size distribution and average size of the TiO_2 nanoparticles.

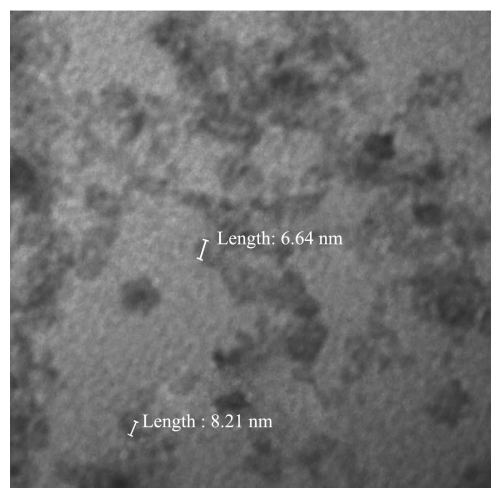


Fig.3 TEM photo of TiO_2 nanoparticles

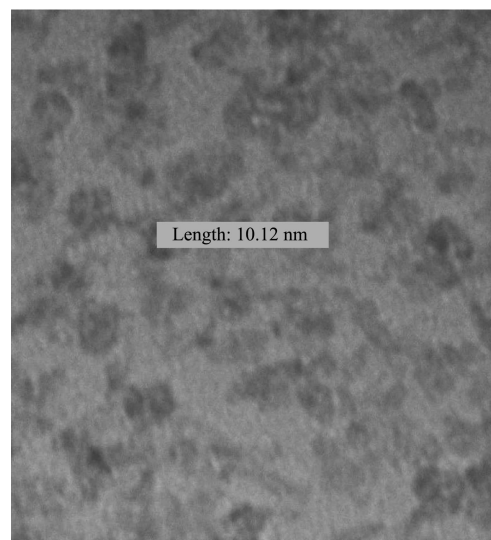


Fig.4 TEM photo of Fe/Ce- TiO_2 nanoparticles

2.5 XPS analysis

The XPS spectra of O1s of TiO_2 (A) and the Fe/Ce- TiO_2 (B) were shown in Fig.5. They were fitted with the non-linear least square fit program using Gauss-Lorentzian peak shapes and three O1s peaks appear af-

ter deconvolution, which were attributed to lattice oxygen(O_L , 530.3 eV), surface hydroxyl oxygen(O_{-OH} , 532.1 eV) and adsorbed oxygen(O_S , 533.6 eV) in TiO_2 ^[29]. According to the handbook of the XPS instrument, the relatively quantitative analysis could be performed by uti-

lizing the XPS peak area of different elements and their own sensitivity factor.

From Fig.5 and Table 2, it could be seen that the amounts of hydroxyl oxygen and adsorbed oxygen on the surface of Fe/Ce- TiO_2 were all increased.

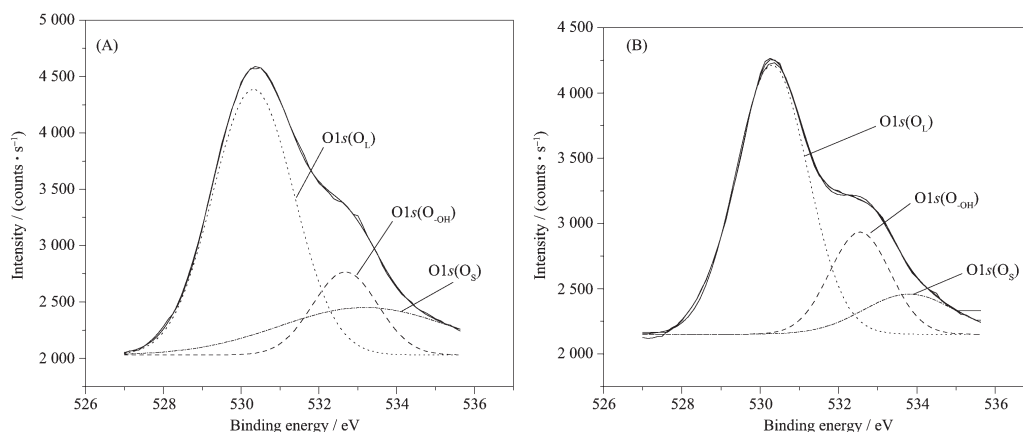


Fig.5 XPS spectra of O1s on the surface of TiO_2 (A) and Fe/Ce- TiO_2 (B) nanoparticles

Table 2 Curve fitting results of XPS spectra for the oxygen species on the surface of different nano-particles

Sample	Percentage of O / %		
	O1s(O_L)	O1s(O_{-OH})	O1s(O_S)
TiO_2	74.6	14.6	10.8
Fe/Ce- TiO_2	66.1	21.1	12.8

2.6 Antibacterial activity

From the data of Fig.6, it is observed that both pure TiO_2 sol and Fe/Ce- TiO_2 sol exhibited higher antibacterial activity against *E.coli*, *B. subtilis* and *S.albus* compared to P25. Fe/Ce- TiO_2 sol show the highest activity against bacteria among three nanometer materials, and the bacteriostatic rates of Fe/Ce- TiO_2 film to three bacteria were above 97% for 6 h. This fact may indicate that the Fe and Ce co-modified is an essential factor to the antibacterial value. The data of Table 3 indicated Fe/Ce- TiO_2 film had better antibacterial activity both under dark and natural light irradiation. Under dark,

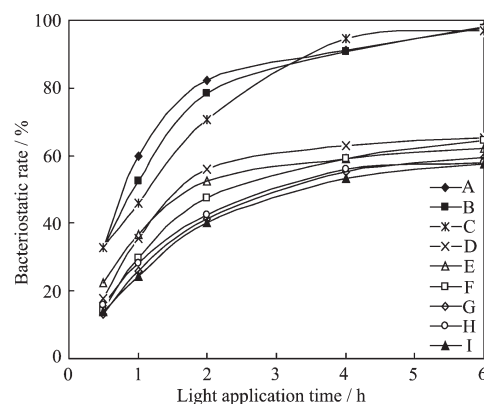


Fig.6 Comparison of the antibacterial activity of Fe/Ce- TiO_2 sol, pure TiO_2 sol and P25

the bacteriostatic rate of Fe/Ce- TiO_2 film was over 70% after 24 h. It may owe to cerium ions on the surfaces of Fe/Ce- TiO_2 particles, because they can take place reactions with some matters in bacterial exterior structure. Under natural light irradiation, the predominance of Fe/Ce- TiO_2 film was significantly expressed. When the natural light irradiation lasted 6 h, the bacteriostatic

Table 3 Bacteriostatic rate of the three nano-materials to bacteria in indoor environment

	Dark			Natural light irradiation		
	6 h	12 h	24 h	6 h	12 h	24 h
P25	20.3	22.1	24.3	60.1	63.5	67.8
Pure TiO_2 sol	40.5	43.2	45.1	63.9	77.3	81
Fe/Ce- TiO_2 sol	55.9	68.1	71.5	91.7	92	94.2

rate was 91.7%. This result indicated that Fe and Ce co-doped had positive action to increase response activity sol particles to visible light.

2.7 Antibacterial mechanism

In the Fig.7, the TEM photos of *E.coli* from(a) to (e) represented the *E.coli* strains during variant phases. The cell in(a) was a whole cell, but there were some holes appearing on the surface of the cell, liking the positions marked by circles, and a few cellular

content was leaked from these holes. The surfaces of cells in (b) and (c) were severely damaged at one or two stations, liking the positions marked by circles in (b) and (c), and the cellular content was lost over 10%. In photo (d), the cell structure was not full, the cell should be dying or dead. Finally, in (e), the cell wall and pericellular membrane had totally disappeared, the cell was dead and the cellular content diffused into surrounding slowly.

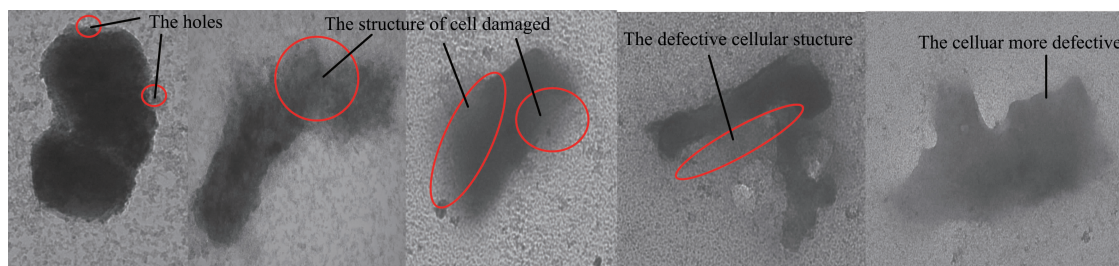


Fig.7 TEM photos of *E.coli* in variant phases

From these TEM photos, it was observed that the cell of *E.coli* was firstly destroyed from some stations on the cellular surface. Then the impairments were exacerbated step by step.

The final result was cell structure disappeared and cell was dead. According to the structure features of cell wall and Fe/Ce-TiO₂ sol particles, the potential antibacterial mechanism was analyzed as following: first, the ferrum ions on the surface of Fe/Ce-TiO₂ particles may be released, and they bonded with teichoic acid and protein of cell wall and pericellular membrane leading to the damage of cell external structure; second, the cerium ions on the surface of Fe/Ce-TiO₂ particles have better antibacterial activity, it could destroy the cell wall structure through ligand reaction with the some matters in the cell wall structure^[30]; in addition, the increase of response ability to visible light created by Fe/Ce co-modified also was an important reason.

3 Conclusions

Fe/Ce-TiO₂ hydrosol were prepared by a microwave-assisted peptization under atmospheric pressure. All the results of characterizations illustrated that paucity ferumiron and cerumiron co-modification could not affect the crystal structure and particle size of TiO₂ sol, but could increase hydroxyl oxygen and adsorbed oxygen on

the surface of TiO₂ particles.

The results of antibacterial experiments showed that Fe/Ce-TiO₂ sol exhibited better antibacterial activity. When the application time was 6 h, the bacteriostatic rate of Fe/Ce-TiO₂ film against three standard strains were above 97%. Moreover, in the experiments simulating indoor environment, the bacteriostatic rates of Fe/Ce-TiO₂ samples were the highest not only under dark but also under natural light irradiation. All the results of antibacterial experiments illustrated that the Fe/Ce-TiO₂ sol had higher broad-spectrum antimicrobial activity.

The antibacterial mechanism of Fe/Ce-TiO₂ sol particles was discussed basically, and the results indicated that Fe/Ce co-doped was an essential factor to the increase of the antibacterial activity.

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