Preparation of (CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ deposited porous TiO$_2$ matrix with highly near-infrared light photocatalytic activity

1 | INTRODUCTION

With the global population growth and the acceleration of industrialization, traditional fossil energy shortage and environmental pollution are becoming severe [1–3]. Development of new green energy along with the environmental pollution control has been acknowledged as the top issues to be urgently solved [4–7]. So far, a large number of studies have shown that photocatalytic materials can reduce water to hydrogen [8, 9], CO$_2$ to organic solar fuel [10], degrade pollutants [11], sterilize, disinfect and so on [12, 13], making such materials the research hotspots in the fields of, energy, environment, and chemistry [14, 15].

Nano titanium oxide (TiO$_2$) has emerged as one of the mostly researched photocatalytic materials highlighted with its low synthesis cost and impressive photo-oxidation capability [16]. However, the shortcomings of nano-TiO$_2$ photocatalysts are its low utilization of visible or even infrared light and ease of agglomeration to cause nano-toxicity, which consequently limit its applications in water/air pollution treatment and biomedical applications. For the former issue, strategy using up-converting rare-earth (RE) luminescent agents to convert near-infrared light into UV light for nano-TiO$_2$ utilization was attempted [17, 18]. For the latter issue, porous matrix coated or composed of nano-TiO$_2$ has been reported in both pollution control [19] and biomedicine [20]. For the aspect of upconversion luminescent materials design, fluorides are efficient hosts of RE ions due to their appropriate energy phonons to produce strong up-converting fluorescence [21]. In particularly, calcium fluoride (CaF$_2$) has been recommended as an efficient up-converting phosphor host, along with its biosafety and biocompatibility [22, 23]. In our previous work, a Ti$^{3+}$/Yb$^{3+}$ co-doped (CaY)F$_2$ nanocrystals have been hydrothermally prepared, in which the incorporation of Y to matrix of CaF$_2$ was explored to enhance the up-converting fluorescence intensity [24]. This material could be stably excited by a 980 nm pump light to generate 360 nm UV light, with intensity controlled by Tm$^{3+}$ and Yb$^{3+}$ content.

In order to take the advantages of porous TiO$_2$ matrix and (CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ upconversion luminescent agent, a (CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ deposited porous TiO$_2$ matrix with highly near-infrared light photocatalytic activity was prepared in current study. The relationship of the material formula and photocatalytic activity was studied. Additionally, the environmental and biomedical potentials of this composite were evaluated using methyl orange (MO) degradation test and fibroblast cytotoxicity study, respectively.

2 | METHODS

2.1 | Chemicals

Yttrium chloride (YCl$_3$), thulium chloride (TmCl$_3$), and ytterbium chloride (YbCl$_3$) were purchased from Youyan Rare Earth Co., Ltd., China. Other chemicals were provided by Tianjin No.3 Chemical Reagent Plant China.

2.2 | Preparation of TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$

Porous TiO$_2$ matrix was prepared using a PMMA template method. First methyl methacrylate (MMA) purified by vacuum distillation was exposed in an Ar environment at 75 °C, followed that 2,2’-azobis[2-methylpropionamidine] dihydrochloride hydrochloride solution (concentration :15 g/L) was dripped and continuously stirred for 4 h to obtain a milky polymethyl methacrylate (PMMA) suspension. Then it was pumped with a 300 nm filter membrane, centrifuged to remove the supernatant and then transferred to a drying oven at 115 °C for 24 h to obtain the PMMA submicron ball stack block.

TiO$_2$ sols using tetrabutyl titanate as precursors were deposited onto PMMA submicron spheres followed by calcination at 450 °C for 4 h to sacrifice PMMA template and induced TiO$_2$ formation. The as-prepared porous TiO$_2$ matrix was soaked into 80 mL aqueous mixture with CaCl$_2$, YCl$_3$, TmCl$_3$, and YbCl$_3$ (Table 1); later, 0.6476 g of ammonium fluoride (NH$_4$F) was added with magnetic stirring to generate a uniform suspension, which was further transferred into a polytetrafluoroethylene (PTFE) autoclave to undergo hydrothermal reaction at 150 °C for 12 h followed by 5 h calcination at 500 °C to obtain TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$.

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TABLE 1  Summary of reactants used to prepare sample

| Nomenclature | TiO$_2$ | YCl$_3$ | TmCl$_3$ | YbCl$_3$ | CaCl$_2$ |
|--------------|--------|--------|----------|---------|---------|
| TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ (1:1) | 1      | 0.3888 | 0.0028   | 0.1398  | 0.5552  |
| TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ (2:1) | 2      | 0.3888 | 0.0028   | 0.1398  | 0.5552  |
| TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ (3:1) | 3      | 0.3888 | 0.0028   | 0.1398  | 0.5552  |

FIGURE 1  A standard curve of the methyl orange solution at 464 nm wavelength photo-excitation ($R^2 = 0.9732$)

2.3  Photocatalyst characterization

The morphology of the samples was examined by field emission scanning electron microscopy (SEM, HITACHI S-4800) with an accelerating voltage of 10 kV. The X-ray diffraction (XRD) patterns of the samples were determined in the range of 2$\theta$ from 5$^\circ$ to 90$^\circ$ on a Rigaku smartlab diffractometer (Rigaku Co., Japan) with Cu K\alpha radiation. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a PHI 5000C ESCA System with Al K\alpha. Photoluminescence (PL) emission spectra were recorded on the Fluorescence spectrophotometer (FL3-22, HITACHI Co. Japan). The UV–visible absorbance of the samples was determined by the UV-3600 Lambda 25 UV–visible-infrared spectrophotometer of PerkinElmer Company, United States of America.

2.4  Photocatalytic activity test

MO solution was chosen as the degradation target. The absorption peak of MO solution is 464 nm. When the concentration is less than 30 mg/L, the absorption rate has a good linear relationship with the concentration. Therefore, MO solution with 15, 10, 7.5 and 5 mg/L concentration is prepared. The absorbance of MO solution with different concentration was determined by the UV-3600 Lambda 25 UV–visible-infrared spectrophotometer of PerkinElmer Company, United States of America.

Using 275 W hard infrared light as the light source, 150 mg photocatalyst was added to 50 mL of MO solution with a concentration of 15 mg/L. The suspension was first stirred in dark for 30 min, so that the photocatalyst reached the adsorption equilibrium for MO. After that, photocatalytic degradation reaction was carried out under infrared light. After removing the photocatalyst particles by centrifugation, 3 mL supernatant was taken and the absorbance of residual MO at different time point was measured by an UV–visible spectrophotometer to track the photocatalysis-associated degradation behaviour of MO.

The kinetic of photocatalysis was studied via capturing the singlet oxygen and hydroxyl radicals by diphenylisobenzofuran (DPBF) and dimethyl sulfoxide (DMSO). Using 275 W hard infrared light as the light source, two kinds of composite materials, 2:1 of 150 mg, were put into DPBF solution with 50 mL concentration of 10$^{-5}$ mol/L. The absorbance of DPBF solution at 412 nm was used to judge the production of the singlet oxygen. Using 275 W hard infrared light as the light source, 150 mg photocatalyst was put into DMSO solution with a concentration of 10$^{-5}$ mol/L. The obtained methyl sulphonic acid was reacted with Fast Blue BB salt solution to form diazo compound, and extracted with a mixture of toluene and n-butanol at 3:1, then the absorbance of the extraction solution was determined at 420 nm for hydroxyl radical production confirmation.

2.5  Cytotoxicity test

The 2.0 mg TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ nanocrystalline powder was accurately weighed by electronic balance, scaled with 2 mL DMEM medium to prepare a 1 g/L mother liquor and sterilized by steam sterilizer for 2 h. The mother liquor was diluted with DMEM cell culture medium of different volume in 5 dosage groups. The final concentration of composite suspension was 0, 25, 50, 100, 150 and 200 mg/mL, respectively. Mouse fibroblasts L929 were inoculated into 96-well plate and incubated overnight at 37 $^\circ$C and 5% (v/v) CO$_2$. After overnight, 10 $\mu$L suspension with different concentration was slowly added to each pore. In the control group, same number of cells and medium volume were applied. Each group was cultured for 24 h at 37 $^\circ$C and 5% (v/v) CO$_2$. Then 96-well plates were taken out, and CCK8 solution was added to each pore. Then the plates were put back into the incubator for 2–4 h. The absorbance of each well (OD) was measured at 490 nm wavelength with a microplate micrograph. The experiment was repeated three times and the average
TABLE 2  
Rating standard between RGR and toxicity

| Relative growth rate RGR (%) | Cytotoxicity grading |
|-----------------------------|----------------------|
| ≥100                        | 0                    |
| 75–99                       | 1                    |
| 50–74                       | 2                    |
| 25–49                       | 3                    |
| 1–24                        | 4                    |
| <1                          | 5                    |

FIGURE 2  
XRD patterns of TiO$_2$, (CaY)$_2$F$_2$:Tm$^{3+}$,Yb$^{3+}$ and TiO$_2$/(CaY)$_2$F$_2$:Tm$^{3+}$,Yb$^{3+}$ (2:1)

value was obtained.

Relative growth rate = $\frac{OD_{\text{Negative control group}}}{100\%}$  
(2)

The 5-point cytotoxicity grading criteria are given in Table 2, with no cytotoxicity at grade 0 and 1, mild cytotoxicity at grade 2, moderate cytotoxicity at grade 3 and 4, and significant cytotoxicity at grade 5.

3. RESULTS AND DISCUSSION

3.1. Characterizations of TiO$_2$/(CaY)$_2$F$_2$:Tm$^{3+}$,Yb$^{3+}$

Figure 2 illustrates the XRD patterns of the porous TiO$_2$, (CaY)$_2$F$_2$:Tm$^{3+}$,Yb$^{3+}$ and TiO$_2$/(CaY)$_2$F$_2$:Tm$^{3+}$,Yb$^{3+}$ (2:1). The (CaY)$_2$F$_2$:Tm$^{3+}$,Yb$^{3+}$ sample shows a typical crystalline diffraction peaks of (CaY)$_2$F$_2$, which can be indexed into (111), (200), (220), (311) planes of (CaY)$_2$F$_2$ (JCPDS NO. 87-0971). It is worth noting that the four peaks around the plane (111) of (CaY)$_2$F$_2$:Tm$^{3+}$, Yb$^{3+}$ may be caused by the appearance of YF$_3$ during calcination. Meanwhile, the TiO$_2$ can be indexed into (101), (004), (200), (105), (204) planes of anatase TiO$_2$ (JCPDS NO. 73-1764), respectively. The XRD patterns demonstrate the coexistence of (CaY)$_2$F$_2$ and TiO$_2$ in the TiO$_2$/(CaY)$_2$F$_2$:Tm$^{3+}$,Yb$^{3+}$ (2:1), and no other phase is found.

The SEM of TiO$_2$ obtained by sol–gel method and PMMA template method can be observed as shown in Figure 3. From Figure 3(a,b), it can be clearly seen that traditional gel method can obtain agglomerated nanoparticles, while the template method obtains the porous structure sample with an aperture of about 300 nm and the connected hole of the size about 100 nm could be seen clearly. Furthermore, structural damage on the pore wall possibly occurred during calcination is seen. These structure features provide mass transfer channels and improve the photocatalytic efficiency.

The morphologies and compositions of surface elements of TiO$_2$/(CaY)$_2$F$_2$:Tm$^{3+}$,Yb$^{3+}$ (2:1) were observed by SEM and TEM. As shown in Figure 4(a), (CaY)$_2$F$_2$:Tm$^{3+}$,Yb$^{3+}$ nanoparticles with an average particle size of 23 nm (it was calculated
with Scherrer equation.) are uniformly loaded on the pore walls of the porous TiO₂ matrix. From Figure 4(b), it can be seen the growth of (CaY)F₂:TiO²⁺,Yb³⁺ (2:1) crystals on surface of TiO₂. In Figure 4(c,d), two lattices spacing of 0.35 and 0.317 nm were seen. The former corresponds to the (101) crystal plane of TiO₂, the latter corresponds to (111) crystal plane of (CaY)F₂. This indicates that TiO₂ matrix has not only porous structure, but also monodisperse grains. (CaY)F₂:TiO²⁺,Yb³⁺ nanoparticles adhere to the edge of porous TiO₂ structure when they are formed.

In order to further confirm the surface element composition, valence state and chemical bond mode of TiO₂/(CaY)F₂:TiO²⁺,Yb³⁺, XPS analysis was performed on them. The results of Yb and Tm are shown in Figure 5. The peak value of Yb 4d at 186.9 eV and Tm 4d at 176.3 eV, which corresponds to Yb⁺³ and Tm⁺³ cations, respectively. Only when the rare earth ion has a +3 valence can it exert its unique energy level transition [25].

3.2 | PL spectra of TiO₂/(CaY)F₂:TiO²⁺,Yb³⁺ nanocomposites

PL spectra of (CaY)F₂:TiO²⁺,Yb³⁺ and TiO₂/(CaY)F₂:TiO²⁺,Yb³⁺ with different mass ratios of TiO₂ to (CaY)F₂:TiO²⁺,Yb³⁺ are presented in Figure 6. For (CaY)F₂:TiO²⁺,Yb³⁺ the UV (360 nm) emissions respond to the ¹I₆ → ³H₆ transitions of Tm⁺³ ions. According to the large absorption cross-section area at 980 nm, Yb⁺³ is effectively excited at this wavelength and in turn transfers energy to Tm⁺³ [26]. After combining TiO₂/(CaY)F₂:TiO²⁺,Yb³⁺ with different mass ratios of TiO₂, the UV emission becomes weak since it was absorbed by TiO₂ (Figure 6).

3.3 | Photocatalytic activity of TiO₂/(CaY)F₂:TiO²⁺,Yb³⁺ nanocomposites

The photocatalytic activities of the as-prepared photocatalysts were evaluated via MO photodegradation experiments under 275 W hard infrared light irradiation and the results are shown in Figure 7. As shown in Figure 7, there is a little concentration reduction of MO in the presence of pure TiO₂. After infrared
irradiation for 10 h, pure TiO$_2$ only degraded 5% of MO. On contrast, the nanocomposites of TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ show impressive degradation effect on MO with 70% of MO degraded by TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ (2:1), which is 14 times higher efficiency than TiO$_2$. This phenomenon indicates that the nanocomposites of TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ display good photocatalytic activity under visible light. With the increase of the content of TiO$_2$ in TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ nanocomposites, the infrared photocatalytic activity of TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ nanocomposites first increased and then decreased. The optimum mass ratio of TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ was 2:1. This may be due to the fact that when the content of up-conversion luminescent materials is too high, TiO$_2$ cannot make full use of the converted UV light effectively.

### 3.4 Near-infrared light photocatalytic mechanism of TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$

The Yb$^{3+}$ in (CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ were excited by near-infrared light had energy level transition and released the energy to Tm$^{3+}$ ion. Then, Tm$^{3+}$ ion absorbed energy will undergo energy level transition and emit 360 nm UV light. Finally, the array porous TiO$_2$ is excited to produce photocatalytic reaction.

The absorbance of DPBF solution at 412 nm varies with the illumination time as shown in Figure 8(a). It can be seen that the absorbance decreases with time, implying there exists singlet oxygen production. On the other hand, the absorbance of the methylene sulphite-BB extract changes with the illumination time as shown in Figure 8(b), confirming the existence of
hydroxyl radical. Therefore, the composite is determined to be excited by both UV and infrared spectra.

### 3.5 Cytotoxicity analysis

Figure 9 is an optical photograph of mouse fibroblasts cultured in 2:1 sample medium for 24 h at different concentrations. After 24 h of cell culture, the morphology of fibroblasts was observed under an inverted microscope. Figure 9(a) is a cell image of a blank group. Figure 9(b) shows the cell image with 50 ppm concentration of composite material. It can be seen that cells grow well in 96-well plate. The morphology of L929 cells has no significant difference compared with the blank control group. The cells are spindle-shaped, and there are a few black spots attributed to composite seen in the field of vision. Figure 9(c,d) shows cell images at concentrations of 100 and 200 ppm respectively. Cells in each group are spindle-shaped or triangular and adhere well to cell wall, indicating the increased concentration of TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ has no obvious influence on cell growth. The OD values obtained by CCK-8 method are as shown in Figure 10, and cytotoxicity results of TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ are shown in Table 3. According to the 5-point cytotoxicity grading criteria (Table 2), the cytotoxicity of TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ was rated as Grade 1 without cytotoxicity.

### 4 CONCLUSION

Porous nano-TiO$_2$ matrix prepared by sacrificing PMMA template was hydrothermally deposited with up-conversion luminescent (CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ nanocrystals to obtain TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$. The characterization and MO degradation results show that TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ are excellent photocatalytic materials under infrared spectra. When the mass ratio of TiO$_2$ to (CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ is 2:1, the best photocatalytic performance can be achieved with the degradation rate of MO 14 times of regular TiO$_2$. In addition, the in vitro cellular test revealed the composite is non-cytotoxic. All results indicate TiO$_2$/(CaY)F$_2$:Tm$^{3+}$,Yb$^{3+}$ nanocomposite may be a promising photocatalyst for environmental and biomedical applications.

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