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Synthesis and Catalytic Performance of Yb^{3+}, Er^{3+} Doped Titanium Dioxide

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Titanium dioxide (TiO_2) nano-materials have been widely applied into solving the environment and energy problems. However, common titanium dioxide materials can only absorb the ultraviolet light in the solar energy. In view of the unique 4*f* and empty 5*d* orbitals, rare earth element own special optical properties like Yb can convert the energy of infrared light into visible light which may be absorbed by Er in the catalytic process. Herein, we successfully doped the rare earth elements of Yb and Er into the TiO_2 nano-material. The photo-catalytic activity of related titanium dioxide nano-material was enhanced through the excitation by visible and infrared light.

Keywords: Titanium dioxide, Yb^{3+}, Er^{3+} doped, Photo-catalysis, Visible and infrared light.

INTRODUCTION

Titanium dioxide (TiO_2) nano-materials have been widely applied into solving the environment and energy problems[1-3] due to its advantages like safety, un-toxicity, stable property, low-cost price and no secondary pollution, *etc*. However, a broader energy-gap of TiO_2 make it can only absorb the ultraviolet part in the solar energy. Considering that only 5 % proportion of the ultraviolet light in whole solar energy, a further applications of TiO_2 are limited[4]. For enhancing the photo-catalytic activity of TiO_2 materials, a number of researchers are working on modified TiO_2 nano-materials through doping technology[5-8]. The purpose of doping is for improving the properties of TiO_2 nano-materials in the visible light. However, the energy of infrared light take 52 % in the whole solar energy[4]. In view of the unique 4*f* and empty 5*d* orbitals, rare earth element have been more focused on the modification of TiO_2 and formation of novel photo-catalytic systems. Hence, we wish to apply the unique up-conversion luminescence of rare metal element into enhancing the absorption of TiO_2 nano-materials on infrared energy.

The up-conversion luminescence means a process which material can absorb low-energy photonics then emit high-energy photonics[9]. When Yb^{3+}, Er^{3+}, Ho^{3+} or Tm^{3+} was doped into ground materials and excited by infrared light, the emitting visible light was enhanced two orders of magnitude. The up-conversion materials become an efficient tools for conversion infrared light into visible light, which have achieved the actually application[11-13]. In our previous works, Yb^{3+}, Er^{3+} doped ZrO_2 nanocrystalline can absorb 980 nm infrared light and emitted visible light[14]. Now, we wish to utilize the Yb^{3+}, Er^{3+} doping TiO_2 nano-particles for increasing the photo-catalytic activity of related titanium dioxide in infrared emitting light.

EXPERIMENTAL

$Er(CH_3COO)_3$, $Yb(CH_3COO)_3$, acetic acid, propyl alcohol, tetrabutyl titanate, ethanol and Rhodamine-B (analytical reagent, AR) were purchased from Beijing Chemical Co., Ltd.; zirconium propoxide (AR) was purchased from Aldrich.

The phase composition was measured by SIEMENS D5005 X-ray powder diffraction (XRD), CuK_α, radiation (λ = 1.5406 Å), tube voltage 40 KV, tube current 200 mA, scan rate 1°/min. Solid ultraviolet data was detected through US Perkin-Elmer Lambda 20 spectrograph (barium sulfate as internal standard). The concentration analysis of Rhodamine-B was used SHIMADZU UV-2450 ultraviolet-visible spectrophotometer.

Preparation of Er^{3+}, Yb^{3+} doped TiO_2 nano-particles: A 40 mL ethanol (Beihua Fine Chemicals Co., Ltd, Beijing, AR) was mixed with 10 mL deionized water, then a certain amount of $Er(CH_3COO)_3$ and/or $Yb(CH_3COO)_3$ was added into above solution. After the solution was clear, a 7.5 mL tetrabutyl titanate (Guangfu Chmicals Co., Ltd, Shanghai, AR) was separately added into the solution under strong stir. This process was completed after three times by dropped 2.5 mL tetrabutyl titanate every hour. Subsequently, through hydrolyzed 24 h and dried over at 80 °C, the TiO_2 powder mixing with resin

was obtained. Through 700 °C calcinating in muffle under N_2, a black powder was harvested. At last, the black powder was calcinated at 550 °C for another 5 h under air atmosphere to yield final product of powder TiO_2. The process of producing pure TiO_2 was similarly with above.

Photo-catalytic decomposition of Rhodamine-B: The reaction of visible and infrared light-catalytic decomposition of Rhodamine-B was carried out in a dark box. The source of visible light was 125 W phillips metal halide lamp ($\lambda > 400$ nm). Each time a 0.05 g catalyst was added into 80 mL Rhodamine-B solution (20 mg/L). After ultrasound sonicated 10 min, the solution was taken into dark box then irradiated under stirring condition. The samples were measured on each 0.5 h. The infrared light source was IR175C type infrared source, phillips. Each time a 0.05 g catalyst was added into 80 mL Rhodamine-B solution (20 mg/L). After ultrasound sonicated 10 min, the solution was taken into dark box then irradiated under stirring condition. The samples were measured on each 1 h.

RESULTS AND DISCUSSION

Different amount of Er^{3+} doped TiO_2: For the doped TiO_2, the crystal form and optical properties were important and related to the photo-catalytic activity. The XRD patterns and solid UV-visible absorption spectra of different amount of Er^{3+} doped in TiO_2 are shown in Figs. 1 and 2, respectively. Fig. 1 shows that the crystal form of 2, 4 and 6 wt % Er^{3+} doped TiO_2 were anatase. For pure TiO_2, the crystal form was a mixture phase of anatase and rutile under the same condition. Hence, the doping Er^{3+} have effect on the crystal growth of TiO_2 and suppressed the appearance of rutile crystal phase. Also, the degree of crystallinity of anatase were firstly increased then decreased as the amount of doping Er^{3+} were increased. The highest degree of crystallinity of anatase appeared on 4 % amount of doping Er^{3+}. At same time, the samples color was changed from red to yellow as following the increase of doping amount. The reason may be because of that the doping rare earth metal in the TiO_2 matrix with amorphous state[10]. Fig. 2 shows that all of the absorption of doping materials were red-shifted about 106 to 540 nm and the absorption peak of pure TiO_2 material was 380 nm. The reason may caused by the doping Er^{3+} showed a little red colour. As the doping amount increasing, the sample's color was increased. The absorption band on 550 and 660 nm may related with the energy level splitting of Er^{3+}.

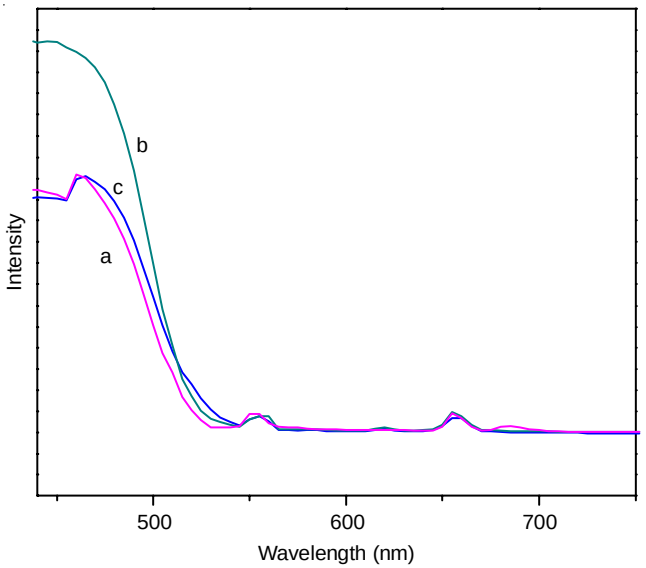

Fig. 2. UV-visible absorption spectra of different amount of Yb^{3+} Er^{3+} doped TiO_2

The catalytic activity of different amount Er^{3+} doped TiO_2 under the irradiation of visible-light were also investigated and the results are shown in Fig. 3. It is observed that the highest catalytic activity appeared on 4 % amount of doping Er^{3+}. The higher Er^{3+} in TiO_2 may cause related higher absorption of visible-light in TiO_2 nano-materials and the best activity emerged in 4 wt. %. However, as the doping Er^{3+} increased further, the red colour in the surface of our fabricated sample became deeper, together with a lower catalytic activity of corresponding samples. The reason may be that a increased Er^{3+} covered a part of TiO_2 surface and the visible-absorption of samples were influenced.

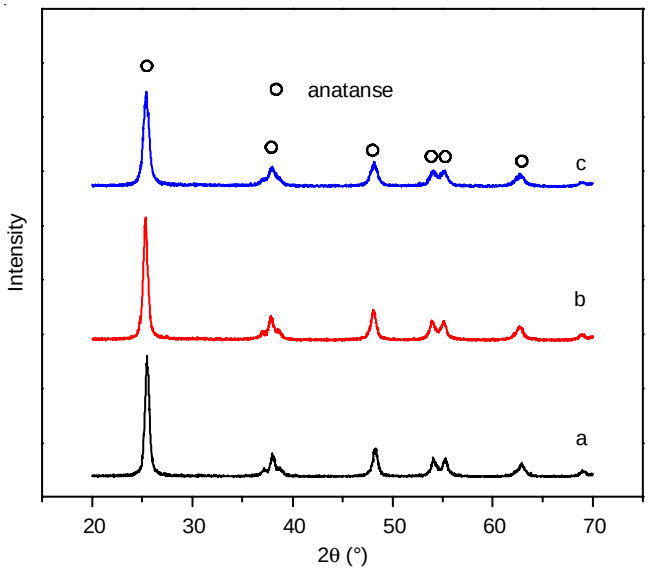

Fig. 1. XRD patterns of different amount of Er^{3+} doped TiO_2. a, b and c represented 2, 4 and 6 wt. % of Yb^{3+} Er^{3+} in TiO_2 nano-materials

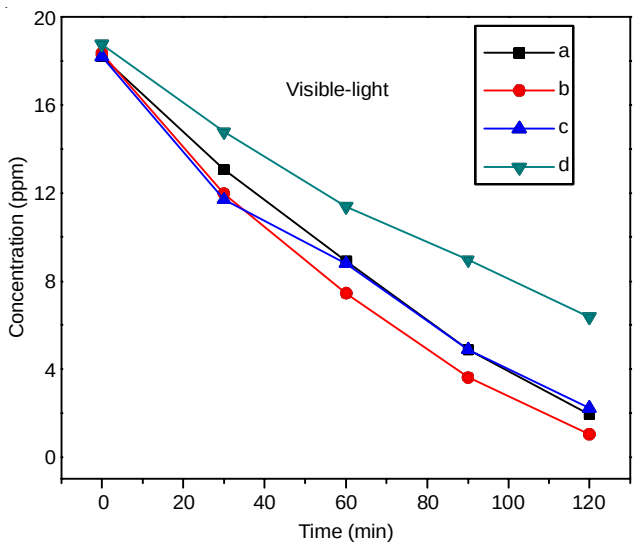

Fig. 3. Activity of different amount of Er^{3+} doped TiO_2 under the irradiation of visible-light a, b, c and d in Fig. 3 represented 2, 4, 6 wt. % and 0 wt. % of Er^{3+} in TiO_2 nano-materials

Different amount of Yb^{3+} doped TiO_2: The crystal form, optical properties and catalytic activity of different amount of Yb^{3+} doped TiO_2 were also investigated. Fig. 4 showed that a XRD patterns of different amount of Yb^{3+} doped TiO_2. All the crystallinity of doped TiO_2 nano-materials were anatase. The doping Yb^{3+} have effect on the crystal growth of TiO_2 and suppressed the appearance of rutile crystal phase. Also, the degree of crystallinity were closely in 2 and 4 wt. % doping amount of Yb^{3+}. The lowest degree of crystallinity appeared in 6 wt. % doping amount of Yb^{3+}.

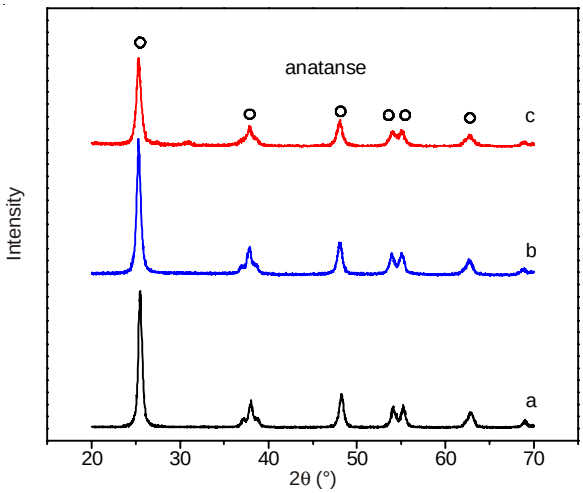

Fig. 4. X-ray diffraction patterns of different amount of Yb^{3+} doped TiO_2. a, b and c represented 2, 4 and 6 wt. % of Yb^{3+} in TiO_2 nano-materials

In Fig. 5, the absorption band in 980 and 1450 nm belonged to Yb^{3+} exciting behaviour in 980 nm and energy level splitting of Yb^{3+} which influenced the absorption in 1450 nm. Compared with the influence of different doping Er^{3+} on the photo-catalytic activity of related TiO_2 nano-materials, we found the best amount of Er^{3+} was 4 wt. % in TiO_2 nano-materials.

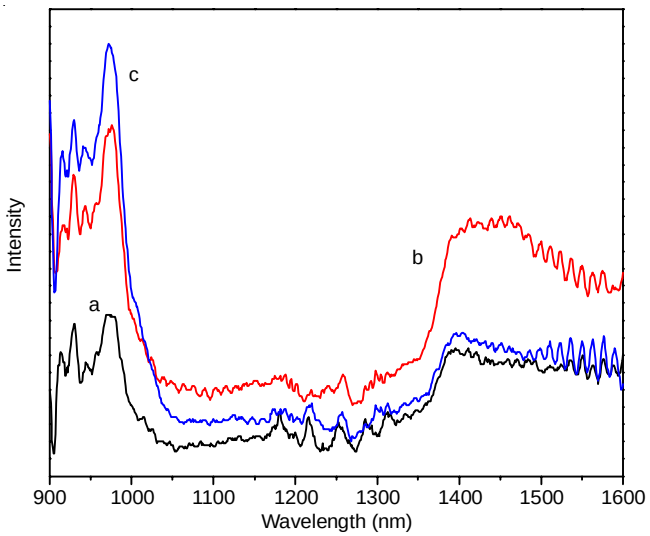

Fig. 5. NIR adsorption spectra of different amount of Yb^{3+} doped TiO_2

Fig. 6 showed that the catalytic activity of different amount of Er^{3+} doped TiO_2 under the irradiation of infrared light. The results indicate that the 2 wt. % amount of Yb^{3+} in TiO_2 nano-materials displayed the highest photo-catalytic activity, which may owing to the big specific surface area.

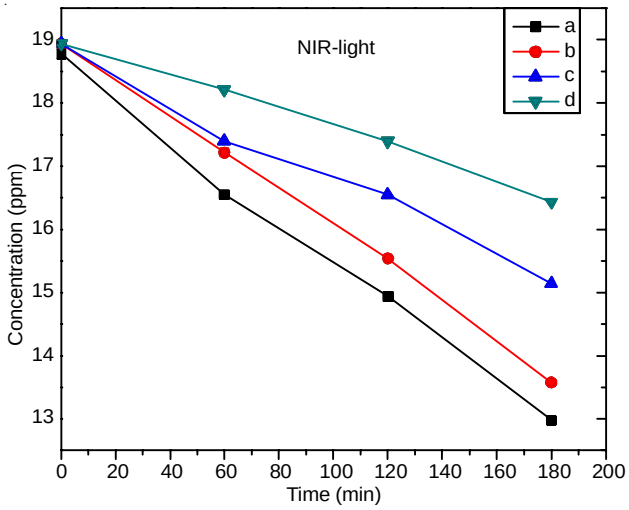

Fig. 6. Activity of different amount of Yb^{3+} doped in TiO_2 under the irradiation of NIR-light

Yb^{3+} Er^{3+} Mix doped TiO_2 nanoparticlew for photo-catalytic activity: Based on the experiment above, a 2 wt. % amount of Yb^{3+} and 4 wt. % amount of Er^{3+} were applied for doped TiO_2. The research of visible and infrared light-catalytic decomposition of Rhodamine-B based on Yb^{3+} Er^{3+} mix doped TiO_2 and pure TiO_2 nano-particles were investigated.

Fig. 7 showed the research of Er^{3+} Yb^{3+} mix doped TiO_2 and pure TiO_2 nano-particles on the decomposition of Rhodamine-B

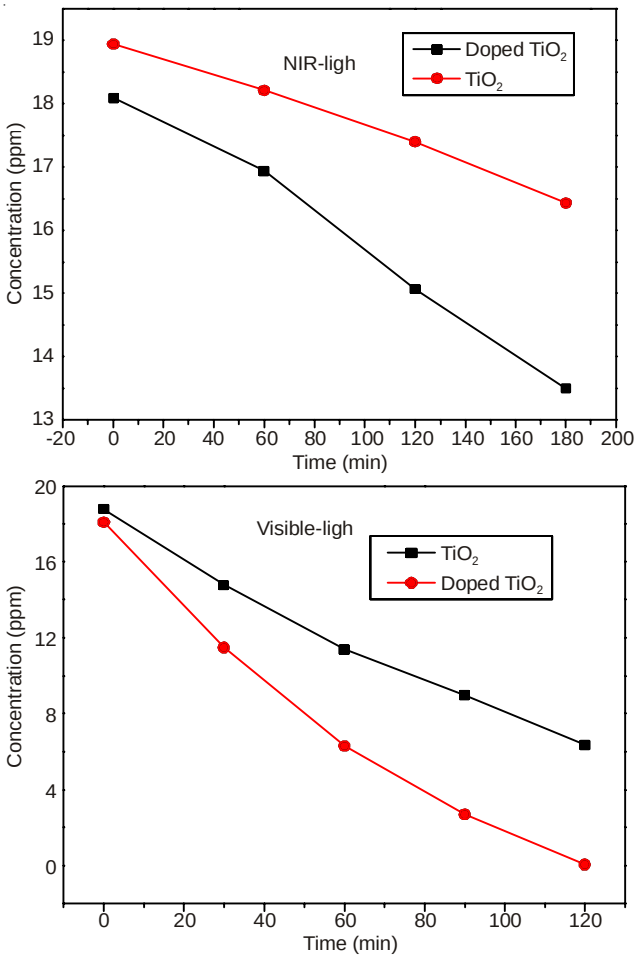

Fig. 7. Decomposition of Rhodamine-B using different doped TiO_2 and pure TiO_2 under the irradiation of visible-light and NIR-light

under a visible and infrared light were investigated. The catalysts used in the two experiments were same. As the $k = -\ln(C/C_0)$, the k_1 value of pure TiO_2 nano-material exciting on visible-light was 8.6×10^{-3} and the k_2 value of Er^{3+}, Yb^{3+} mix doped TiO_2 nano-mateiral was 1.59×10^{-2}. After the same calculation, the k_3 value of pure TiO_2 nano-material exciting on infrared-light was 7.5×10^{-4} and the k_4 value of Er^{3+}, Yb^{3+} mix doped TiO_2 nano-mateiral was 1.6×10^{-3}. As $k_4/k_3 > k_2/k_1$, the capability of Er^{3+} Yb^{3+} mix doped TiO_2 nano-materials on enhancing the photo-catalytic activity has been demonstrated.

Conclusion

By utilizing the unique up-conversion property of rare earth elements, we have successfully doped the Yb and Er metals into TiO_2 nano-materials. A doping Yb increased the absorption of TiO_2 nano-material on infrared light and the doping Er increased the absorption of TiO_2 nano-material on visible light. The Er^{3+} Yb^{3+} mix doped TiO_2 nano-materials can increase the photo-catalytic activity in visible and infrared region and enhance the utilization on solar energy. The Er^{3+} Yb^{3+} mix doped TiO_2 nano-materials may have a potential application on environmental pollution treatment and photo-electricity energy.

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