Preparation and NIR light-driven photocatalytic properties of \( \beta \)-NaYF\(_4\):Yb\(^{3+}, \ Tm\(^{3+}/ZnO\) core-shell composites

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Abstract. A novel UV/NIR light-driven \( \beta \)-NaYF\(_4\):Yb\(^{3+}, \ Tm\(^{3+}/ZnO\) core-shell composites were prepared via microwave assisted hydrothermal technology. The results of characterize indicated that the \( \beta \)-NaYF\(_4\):Yb\(^{3+}, \ Tm\(^{3+}/ZnO\) was obtained by loading ZnO on the surface of \( \beta \)-NaYF\(_4\):Yb\(^{3+}, \ Tm\(^{3+}, \) which could efficiently absorb the UV emission light via upconversion process of \( \beta \)-NaYF\(_4\):Yb\(^{3+}, \ Tm\(^{3+}, \). The degradation of MB using \( \beta \)-NaYF\(_4\):Yb\(^{3+}, \ Tm\(^{3+}/ZnO\) particles as photocatalyst under irradiation of simulated sunlight without UV light showed photocatalytic activity of \( \beta \)-NaYF\(_4\):Yb\(^{3+}, \ Tm\(^{3+}/ZnO\) could be driven under irradiation of NIR light.

1. Introduction

For the past few years, the rapid development of science and technology has brought convenience to mankind, but also brought about acute environmental pollution and energy shortages. The development of efficient pollution control technology using renewable clean energy has become an urgent problem. Semiconductor photocatalysis technology has attracted the special attention of environmental scientists due to their high photodegradation efficiency to toxic chemicals in environment. Among various photocatalysts, TiO\(_2\) and ZnO has been studied and used extensively due to their high photodegradation efficiency, low cost, high chemical stabilities and safety toward both human and environment [1-5]. Compared with TiO\(_2\), ZnO exhibits higher photocatalytic performance for certain organic pollutants [6]. Unfortunately, ZnO and TiO\(_2\) with wide bandgaps of 3.47 and 3.2 eV respectively, their photocatalytic activities can only be driven under ultraviolet (UV) light irradiation [7]. It is generally known, the UV spectrum only occupies 5\% of the solar energy, while visible (Vis) spectrum (about 48\%) and near-infrared (NIR) spectrum (about 47\%) account for approximately 95\% of solar light. Scilicet, about 5\% of the sunlight can be used to stimulate the photocatalysis of TiO\(_2\) and ZnO, which greatly limit the development and application of photocatalysis technology[8]. Thus, it is very important to develop advanced photocatalysts that could take full advantage of the solar energy.

In order to extend spectral response range of solar light and achieve the efficient photocatalytic performance of TiO\(_2\) and ZnO under irradiation of sunlight, diverse ways, such as semiconductor coupling [9], metal and non-metal doping [10,11], has been adopted to extend the absorption range of photocatalysis to the Vis spectrum region. However, the efficiency of using NIR light to actuate photocatalytic activity remains a big challenge [12]. With the development of materials science, nanomaterials with upconversion (UC) emission property have been discovered and studied widely [13]. UC nanomaterials can effectively transform NIR into UV light. Preparation of UC nanocrystals and semiconductors composites is considered to be the effective way to utilize NIR light in the field of photocatalysis [14]. So far, different morphology and structure of UC nanoparticles have been synthesized, and the hexagonal phase \( \beta \)-NaYF\(_4\):Yb\(^{3+}, \ Tm\(^{3+} (UCP)\) crystals have proved to be the best
UC materials [15].

In this case, we prepared the β-NaYF₄:Yb³⁺, Tm³⁺/ZnO core-shell (UCP/ZnO) composites via microwave-assisted hydrothermal method [16]. The composites were used as photocatalyst to decompose methylene blue (MB) under the simulated solar light irradiation with or without UV light via adding a UV filter. The research proves the microsized hexagonal UCP rod can convert efficiently NIR light to UV, which drive the photocatalytic activity of ZnO coated on UCP/ZnO.

2. Experimental

2.1 Synthesis of β-NaYF₄:Yb³⁺, Tm³⁺/UCP

UCP micro-rods were prepared according to the methods mentioned before [16-18]. In a typical synthesis, Y(NO₃)₃, Yb(NO₃)₃ and Tm(NO₃)₃ with a molar ratio of Y/Yb/Tm=80:19.5:0.5 were added to 10 ml, 0.2 mol L⁻¹ EDTA solution and kept stirring for 1 h under 60 °C, then 10 ml, 1 mol L⁻¹ NaNO₂ and 1 mol L⁻¹ NH₄F solution was added to the reaction system under stirring for 1 h. The suspension gotten from the co-precipitation step was transferred to a 30 mL pressure reactor, and exposed to MW radiation for 1 h at 200 °C under stirring. The obtained particles were centrifuged and washed with ethanol and deionized water. The UCP micro-rods were gotten via finally dried at room temperature under vacuum oven at 60 °C overnight.

2.2 Synthesis of β-NaYF₄:Yb³⁺, Tm³⁺/ZnO core-shell (UCP/ZnO) composites

The UCP/ZnO composites were prepared as follows [19,20]: Zn (acac)₂ (1mmol), 20 mL benzyl ether, 3 mL oleic acid and 3 mL oleylamine were mixed in a 50 mL round bottom flask and stirred under a flow of argon gas. The mixture was heated to 150 °C for 1.5 h, and then the 1mmol UCP was slowly added into it. After then, under an argon atmosphere, the mixed solution was stirred and heated to 200 °C for 1 h, then 250 °C for 30 min. The mixture was cooled naturally to normal temperature. The samples were obtained from the solution by centrifugation, then the particles were washed with ethanol and deionized water. The UCP/ZnO composites were obtained dried at 60 °C for 12 h, then calcined at 400 °C for 2 h in argon protection.

2.3 Characterization

The morphology pictures of UCP/ZnO were obtained by scanning electron microscope (Quanta 200, Holand) with an voltage of 20.0 kV and transmission electron microscope (FEI TECNAI ) operating at 200 kV accelerating voltage. The crystal structure of UCP/ZnO composites was demonstrated using X-ray diffractometer (Cu Kα radiation, 30 kV, 30 mA, λ=0.154 Å). The UC emission spectrum were noted down by fluorescence spectrophotometer (Hitachi F-4600), which was equipped with an R3788 photomultiplier tube and 980 diode laser. The UV–visible diffuse reflectance spectrum (UV-DRS) of UCP/ZnO composites was recorded using ultraviolet–visible spectrophotometer (TU-1901, Persee, China).

2.4 Photocatalytic performance measurement

The photocatalytic performance of UCP/ZnO composites were evaluated via the photocatalytic degradation of MB. Xe lamp(1 kw) was used as a stimulated light source, and UV spectrum of Xe lamp was removed via the addition of an UV filter. During the experiment, 20 mg UCP/ZnO were added to 50 mL of 15 mg/L MB solution. The suspensions were stirred constantly for 2 h no irradiation to ensure adsorption/desorption equilibrium of MB on UCP/ZnO. The reaction temperature was set at 25°C. The suspension liquid was taken at regular intervals, and supernatant used for analysis was obtained by centrifugation (3000 r.p.m., 5 min) and filtration (0.2 μm membrane syringe filter). The change of MB concentration during the reaction was tested by UV spectrophotometer. Each group of the experiments was repeated three times and average values were used as results.
3. Results and discussion

3.1 Morphology and structure characterization

The morphologies of UCP and UCP/ZnO composites are shown in Figure 1. The SEM image of UCP shown in Figure 1(a) is similar to the early reports [1,2], which exhibits the hexagonal nanorods. The surface of the nanorods is smooth, and has clear edge, the diameter or length range from 1 to 3 µm or from 4 to 8 µm, respectively. When ZnO particles are coated on the surface of UCP/ZnO, the surface of UCP/ZnO composites become much rougher as shown in Figure 1(b), and the TEM image of the layers of UCP/ZnO is shown in the inset of Figure 1(b), which indicates the formation of UCP/ZnO is core-shell microstructure. The crystal structure of the as prepared UCP/ZnO were examined by XRD. As shown in Figure 2, the XRD patterns of UCP/ZnO matches well with that of hexagonal phase β-NaYF₄:Yb⁺, Tm³⁺ (JCPDS no.28-1192) and the diffraction peaks of ZnO (JCPDS no.79-0208), respectively. This result indicates that the UCP/ZnO composites are core-shell structure formed with hexagonal phase UCP and ZnO with hexagonal wurtzite structure.

![Figure 1. SEM images of UCP (a) and UCP/ZnO (b) (Inset:TEM images of the layer of UCP/ZnO)](image)

![Figure 2. XRD patterns of UCP/ZnO](image)

![Figure 3. The upconversion processes of UCP/ZnO under excitation at 980 nm [20]](image)

3.2 Upconversion spectrum and UV-Vis spectra

The UCP rods is a classic UC material that can convert NIR ligh into higher energy UV light via physically successive energy transfer process of lanthanide ions [7,19-21]. Figure 3 [20] illustrates the processes of UC luminescence in a Yb³⁺–Tm³⁺ co-doped system. The NIR light of 980 nm could be absorbed by Yb³⁺ ions, some energy transfers from Yb³⁺ to Tm³⁺, then provide spectra emissions. As shown in Figure 4, three UV emission peaks located at 291, 345 and 361 nm, two blue emission peaks at 451 nm and 476 nm were found, and attributed to the transitions of Tm³⁺ ions corresponding to ¹I₆/²H₆, ¹I₆/²F₄, and ¹D₁/²H₆, ¹D₁/²F₄ and ¹G₁/²H₆, respectively. In the spectra of UCP/ZnO composites, the intensities of the peaks at 291, 345, and 361 nm decreased significantly while compared with the peaks at 464 and 474 nm. To further ascertain the cause of the decreased UV emissions of UCP/ZnO, the UV-vis spectra of UCP/ZnO was tested, as demonstrated in Figure 5. The absorption peak started at near 387 nm, which correspond to the spectrum of 291, 345 and 361 nm. Therefore, we can conclude that the emission spectrum of 291, 345 and 361 nm generated by the UC process of UCP has been absorbed
partially by ZnO coating.

Figure 4. PL spectra of UCP and UCP/ZnO composites under 980 nm irradiation at room temperature

Figure 5. UV-Vis spectra of UCP/ZnO

3.3 Photocatalytic performance of UCP/ZnO composites

To test the effect of the UC material on the photocatalytic performance of UCP/ZnO composites under NIR irradiation, photocatalytic degradation experiment of MB using UCP/ZnO, UCP and ZnO as catalyst were performed under irradiation of simulated solar light or simulated sunlight with UV removed. As shown in Figure 6, the concentration of MB has almost no change in pure MB solution and adding the UCP of MB solution under irradiation of simulated solar light with UV region or without UV region for 5 h. It means that MB does not undergo photolysis and the UCP have no photocatalytic activity. In Figure 6(a), under simulated sunlight, in presence of ZnO nanoparticles and UCP/ZnO composites, the concentration of MB decreased obviously, and the MB removal efficiency was better after adding UCP/ZnO. Whereas, indicated in Figure 6(b), when UV from simulated solar light was removed by adding a UV filter, the photocatalytic degradation ratio of UCP/ZnO for MB is about 45% within 5 h. Meanwhile, the decomposition ratio of ZnO for MB decreased obviously, almost 10%. The cause of these results was photocatalytic activity of ZnO can only be excited by UV light. ZnO will lose its photocatalytic activity when the UV is removed from the simulated sunlight. However, UCP can transfer the NIR light from simulated sunlight into UV light because of the UC property, which activate the photocatalytic activity of ZnO loaded on the surface of UCP/ZnO.

Figure 6. Photodegradation of MB under simulated solar light irradiation

(a) with UV
(b) without UV region

4. Conclusions

The UCP/ZnO core–shell composites have been prepared by a microwave-assisted high temperature hydrothermal way. SEM, XRD, the PL spectrum and the UV-vis spectrum were used to demonstrate the composites. The results of characterize indicated that the UCP/ZnO composites were prepared by loading ZnO nanoparticles on the surface of UCP. PL spectra of UCP and UCP/ZnO showed that ZnO could efficiently absorb the UV emission light via UC process of UCP. The degradation of MB using β- UCP/ZnO particles as photocatalyst under irradiation of simulated sunlight without UV light indicated photocatalytic activity of UCP/ZnO could be driven under irradiation of NIR spectrum from
simulated sunlight. The NIR light-driven photocatalyst obtained in this research may have a significant prospect on the utilization of solar energy.

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