CeF_3 Fullerene-like Nanoparticles: Synthesis, Upconversion Properties and Application in Photocatalysis Reduction of CO_2

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ABSTRACT

The hexagonal phase CeF_3 particles with fullerene-like structure were synthesized using the microwave-assisted hydrothermal method (M-H). The fluorescence spectrum (PL) showed that the sample could emits light of 304nm and 324nm after excitated by light of 524 nm, 554 nm, 780 nm and 850 nm, which could achieve a large range of energy upconversion. The up-conversion luminescence mechanism of CeF_3 was proposed to a multi-photon simultaneous absorption and emission, and the formation mechanism of the hollow structure was supposedly an Ostwald Ripening process. Moreover, the sample was composited with TiO_2 to initiate a photocatalytic reduction of CO_2 experimental under visible light (λ>515nm).

Keywords: Fullerene-like CeF_3, nanoparticles, upconversion luminescence, TiO_2/CeF_3 composite, catalytic reduction of CO_2

1 INTRODUCTION

As one of rare-earth fluoride, CeF_3 exhibits good luminescence property, lower phonon-energy and special lamellar structure. So it is regarded as a most promising candidate for the materials in high-energy physics, biomarker, and lubricant [1-3]. However, CeF_3 was rarely considered as an up-converting material in the past years because Ce^{3+} is lack of corresponding energy levels in visible light or near infrared area. Recently, Qiu et. al, have demonstrated the up-converting luminescence of Ce^{3+} droped in different host material excited by simultaneous absorption of three infrared photons using an infared femtosecond laser[4-6]. This discovering suggest that Ce^{3+} droped compounds can be good candidates for near-infrared to ultraviolet up-converting Phosphor. Compared with doped materials, the molar concentration of Ce^{3+} can be 100% in CeF_3 crystals, and the CeF_3 is also an excellent ground host material, its' luminous performance worth studying.

Furthermore, as reported by literature [7], the shapes of the materials can influence the properties of CeF_3 with nano size and lead to different application. Among various nanostructures, fullerene-like structure (IF) with the hollow cavities inside have attracted increasing attention because of their novel application value. Currently, This hollow CeF_3 can be prepared by using hydrothermal method [8] or introducing F^- to a classical Belousov-Zhabotinsky (BZ) oscillating reaction in the bromate-citricacid-Ce(IV) - H_2SO_4 system [9]. In this paper, IF CeF_3 with up-conversion luminescence property was prepared successfully based on the microwave-assisted hydrothermal treatment. Moreover, anatase TiO_2 was synthetized on the CeF_3 surfaces by using microwave-assisted alcohol-thermal method to prepare the IF CeF_3/TiO_2 composite. Then the IF CeF_3/TiO_2 was used in photocatalytic reduction of CO_2 experimental and was proved to exhibit visible-light catalytic activity.

2 EXPERIMENTAL SECTION

2.1 Preparation

In a typical procedure, 1 mmol $Ce(NO_3)_3 \cdot 6H_2O$ was dissolved in 15 mL distilled water, then 15 mL of aqueous containing 9 mmol NH_4F was dripped into the solution under stirring. After additional agitation for 30 min, the suspension was transferred into a Teflon-lined vessel then experienced an MH treatments for 30 min at 180 ^oC. As the reaction system was cooled to room temperature naturally, the precipitates were separated by centrifugation, washed with deionized water and ethanol respectively, then dried in air at 60 ^oC for 12 h to obtain the IF CeF_3 nanoparticles.

When prepare the IF CeF_3/TiO_2 composite, 0.4g IF CeF_3 obtained above was dispersion in a solution with 7.64 mL ethanol and 7.83 mL acetic acid by stirring and ultrasonic mixing to prepare a turbid liquor. Then another solution with 6.67 mL butyl titanate and 7.64 mL ethanol was injected into the turbid liquor with a rate of 0.05 mL/ s under stirring. The final mixed liquor experienced same MH processing, centrifugal washing (only used ethanol) and drying processing as the preparation of IF CeF_3. The dry powder was annealed in 300 °C for 3 h and 450 °C for 30min with the heating rate of 5 °C/ min to obtain the IF CeF_3/TiO_2 composite. Pure TiO_2 could be synthesized as this process was repeated without adding IF CeF_3.

2.2 Characterization.

The Crystalline phase of samples was identified by X-ray diffraction (XRD, Bruker D8, Cu Kα, λ=0.15406 nm). The general morphologies were observed using a field-emission scanning electron microscope (SEM, JSM-6390A) with energy-dispersive X-ray (EDX) analysis, and a transmission electron microscope (TEM, JEM-100SX) with selected area electron diffraction (SADE) analysis. The Photoluminescence spectral (PL) were measured on a fluorescence spectrophotometer (Hitachi F-7000, equipped with a 150 W xenon lamp as the excitation source).

3 RESULTS AND DISCUSSION

3.1 Structure and Morphology

Fig.1 shows XRD patterns of the as-prepared IF CeF_3, TiO_2 and IF CeF_3/TiO_2 composite samples. The high and sharp peaks in the patterns indicate that all of the samples are well crystallized. According to the JCPDS standard, the IF CeF_3 and TiO_2 can be easily indexed as pure hexagonal phase CeF_3 (JCPDS No.38-0452, Fluocerite) and pure Anatase TiO_2 (JCPDS No.21-1272, Fluocerite) respectively. The pattern of CeF_3/TiO_2 composite includes both the diffraction peaks of IF CeF_3 and TiO_2 without other impurity peak, that illustrate the compounding would not change the crystalline phase and chemical properties of TiO_2 or IF CeF_3. Scherrer crystallite sizes of IF CeF_3 and TiO_2 in their pure substance are calculated to 20.9 and 24.4 nm, while their sizes in IF CeF_3/TiO_2 composite are 19.7 and 37.2 nm.

The morphology of the as-prepared IF CeF_3, TiO_2 and IF CeF_3/TiO_2 composite is illustrated in Fig.2. The TEM image of IF CeF_3 sample (Fig.2A, 2B) shows the nano hollow sphere-like or hollow rod-like CeF_3 with good dispersibility. The sphere-like nanoparticles have a diameter of about 30 nm, while the rod-like nanoparticles have a length of 30 nm and a diameter of about 15 nm. The EDXA analysis indicates that the mole fraction of Ce and F in this IF CeF_3 are 75.24% and 24.76%, which is in agreement with a molar ratio of 1:3. The SADE pattern (Fig. 2C) of the sample, obtained from a single hollow nanoparticle reveals polycrystallinity. It can be supposed that the hollow structures could result from the Ostwald ripening process. Fig.2D, 2E are the SEM images of the IF CeF_3 and TiO_2 respectively. It can be observed easily that the IF CeF_3 sample is composed with many uniform nano particles, but the TiO_2 sample is composed with big agglomerations of different size. In SEM image of IF CeF_3/TiO_2 composite (Fig.2F), the feature of IF CeF_3 is unseen, which could be due to that CeF_3 is well intermixed or coated with TiO_2.

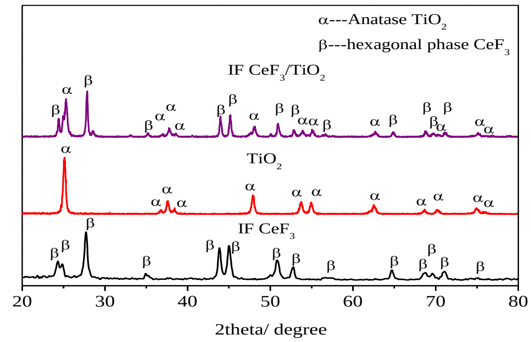


Figure 1. XRD patterns of IF CeF_3, TiO_2 and IF CeF_3/TiO_2 composite

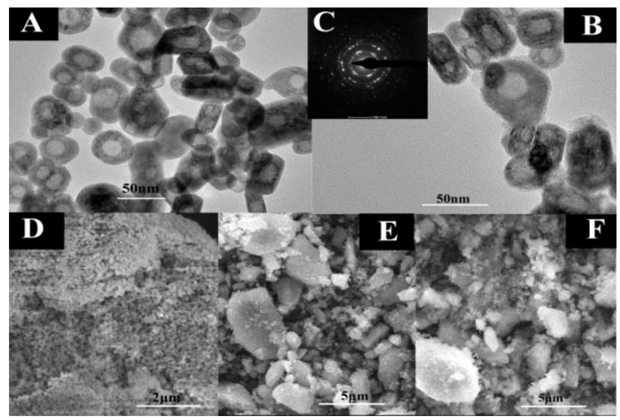
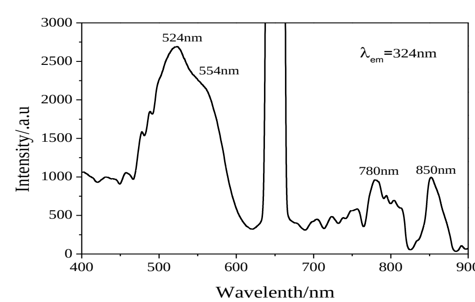


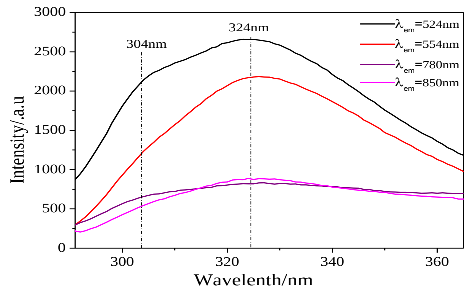
Figure 2. TEM images (A, B), SADE pattern(C), SEM image(D) of IF CeF_3 sample and SEM images of TiO_2 (E), IF CeF_3/TiO_2 sample (F).

3.2 Up-Conversion Luminescence Properties

Figure 3 show the up-conversion luminescence excitation and emission spectra of the IF CeF_3 sample. It can be observed that under the excitation of 524 nm, 554 nm, 780 nm and 850 nm, the IF CeF_3 can emit UV light of 304 nm and 324 nm. The luminescent intensity weakened with the increasing in wavelength of exciting light. This process can achieve large scope of energy up-conversion from visible and near-infrared light to UV light.



(a)



(b)

Figure 3. Up-conversion luminescence excitation (a) and emission (b) spectra of the IF CeF_3 sample

3.3 Photocatalytic Properties

The visible-light catalytic activity of samples was measured by photocatalytic reduction of CO_2 with water under the light which wavelength greater than 515nm. Figure 4 shows the yield-time changes of major product methanol in this reaction when used different samples as catalytic respectively. It can be seen clearly that IF CeF_3/TiO_2 composite has obvious activity while IF CeF_3 or TiO_2 are not. The corresponding methanol yield increases quickly and reaches to 169.23 μmol/ g-cat at 3h when the CeF_3/TiO_2 composite is used as catalytic. The result illustrate that the visible light (λ>515 nm) catalytic activity of TiO_2 could be initiated under the existence of CeF_3, and the spectral response range of TiO_2 is extend. That should due to that TiO_2 can absorbs the UV light converted from visible light by IF CeF_3 to exhibits a catalytic effect.

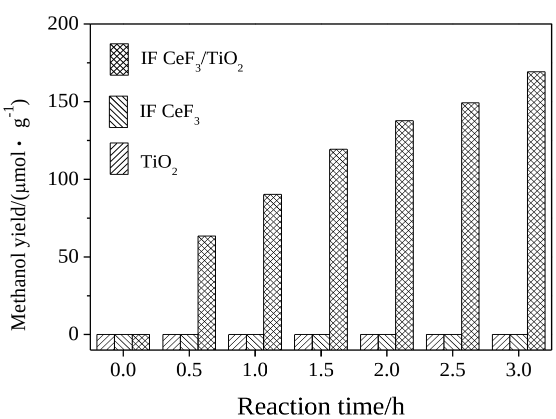


Figure 4. Methanol yield of photocatalytic reaction of CO_2 under visible light irradiation (λ>515 nm) using the IF CeF_3, TiO_2, and IF CeF_3/TiO_2 as catalyst respectively.

3.4 The Mechanism of Up-Conversion Luminescence

In order to research the up-conversion process, the down-shifting luminescence excitation and emission spectra of the IF CeF_3 sample also be detected (Figure 4). The result shows that the IF CeF_3 can also emit light of 304 nm and 324 nm after excited by ultraviolet light of 260 nm and 280 nm. That is attributed to electrons' transition from the $^2F_{5/2}$ ground state to different components of the 5d states in Ce^{3+} split by the crystal field. The phenomena demonstrate obvious properties of broad-band absorption and emission, which is in consistence with most references [10-12].

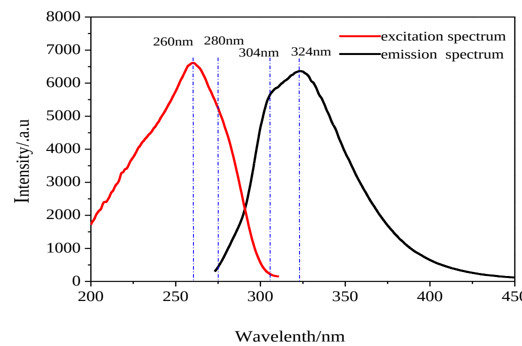


Figure 5. Down-shifting luminescence excitation spectra and emission spectra of the IF CeF_3

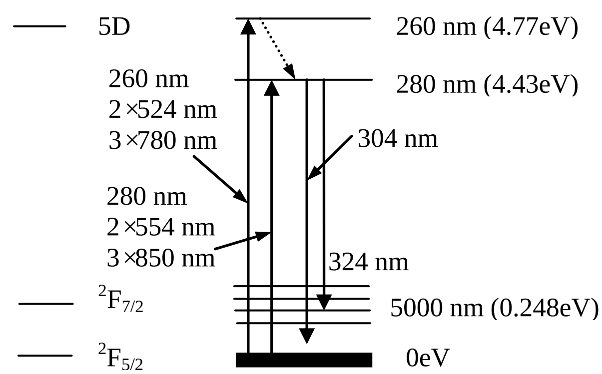


Figure 6. Up-conversion luminescence process of the IF CeF_3 sample

It is apparent that the exciting and emitting peak of up-conversion are similar to that of the down-shifting in shape and position, can be indicated to the transition of the Ce^{3+} electronic between 5d and 4f level. Through analyzing the exciting energy of 260 nm is twice and three times as much as the excitation light of 524 nm, 780 nm respectively. Meanwhile, the lights of 524 nm, 554 nm, 780 nm, 850 nm were not found in the emission spectra, it is supposed that there were not corresponding intermediate levels between 4F and 5D level. According to above analysis, the luminescence mechanism should be deduced to a multi-photon simultaneous absorption. This phenomenon could be considered that more than one photon are absorbed at the same time, which result in electron-transitions from the initial state to final state, just through the hypothetical intermediate state.

The concrete process is showed in figure 6. At first, the electron located on the ground state ($^2F_{5/2}$) is excited to the energy level of 4.43 eV or 4.77 eV after absorbing two photons of 525 nm or three photons of 780 nm at the same time, then resulting the UV emission of 304 nm or 324 nm after lost some energy reacting with surrounding crystal field.

4 CONCLUSION

Fullerene-like nano CeF_3 with up-conversion luminescence property have been successfully fabricated through a facile and effective microwave hydrothermal method. When excited by the light of 524 nm, 554 nm, 780 nm and 850 nm, this IF CeF_3 could emit the light of 304 and 324 nm, the corresponding luminous mechanism could be conjectured as the multi-photon simultaneous absorption luminescence. By using a microwave-assisted alcohol-thermal method and annealing, the CeF_3 was composited with anatase TiO_2 to improve the visible-light catalytic activity of the latter. The result of photocatalytic reduction of CO_2 showed that the CeF_3/TiO_2 composite has an obvious catalytic effect under visible light.

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