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Novel UV–vis-driven photocatalysts of CeF_3/TiO_2 nano-sheet film with upconversion properties for enhanced photocatalytic activity

Jun Wan [a,1], Lin Sun [a,1], Enzhou Liu [a], Jun Fan [a,*], Xiaoyuan Hu [b], Chenchen Pu [a], Juan Li [a], Xiao Du [a]

[a] *School of Chemical Engineering, Northwest University, Xi'an 710069, PR China*
[b] *School of Physics, Northwest University, Xi'an 710069, PR China*

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ABSTRACT

Upconversion photocatalysts have the potential to extended utilization of sunlight and enhance the photocatalytic performance. A novel hybrid architecture of CeF_3/TiO_2 nano-sheet film (NSF) was synthesized via a facile one-step microwave-hydrothermal synthesis. The luminescence agent of CeF_3 nanodisks were deposited homogeneously on the surface of the TiO_2 NSF. The CeF_3/TiO_2 NSF composite materials show obvious photodegradation of MB under visible light as well as ultraviolet light, resulting in enhanced photocatalytic activity in the UV–vis bands solar spectrum due to the efficient upconversion emissions of CeF_3. Additionally, a photocatalytic mechanism of CeF_3/TiO_2 NSF was proposed.

1. Introduction

Extended utilization of sunlight from ultraviolet (UV) to visible (vis) and nearinfrared (NIR) light is an attractive issue for the photocatalyst development [1,2]. Nowdays, the common TiO_2-based photocatalysts reported are still limited to ultraviolet (UV) light that only occupies ca. 5% in the solar spectrum, while visible light (~48%) and near infrared (NIR) light cannot be effectively utilized [3]. Intensive investigations have been carried out to extend light utilization of TiO_2, including coupling with other narrow band gap semiconductors [4], metal ions or non-metal elements doping [5,6] and deposition of noble metals [7]. However, they are inevitably confronted with several disadvantages, such as poor stability, relatively low visible light absorption and the difficult separation of electron-hole pairs [8–10]. Combination of upconversion materials (UCM) have attracted tremendous interest in recent years to increase the utilization of light for TiO_2 photocatalysts [11–13]. Nevertheless, the reported UCM are mostly excited by NIR light, few attention has been paid to the development of visible-driven TiO_2 upconversion photocatalysts aiming to improve light utilization of solar energy in the visible region.

Fluorides have been proved to be promising upconversion luminescence agents, and some fluoride compounds, such as lanthanide-doped CaF_2 [14], YF_3 [15] and $NaYF_4$ [16], have been reported in the synthesis with TiO_2 photocatalysts to increase the light harvesting. However, there are few reports that focus on the upconversion fluorescence properties of CeF_3 and the synthesis of photocatalysts for the CeF_3-enhanced photocatalytic system. Generally, the particle size, crystal structure and contact form have a significant influence on the properties of upconversion photocatalysts, such as luminescence efficiency and energy transfer from the UCM to the TiO_2 [17,18]. In our previous work, we have introduced the luminescence process of CeF_3, and CeF_3/TiO_2 particles are synthesized in chaotic mixed form [19]. Therefore, in this work we intended to extend our previous work by directly in-suit forming CeF_3 with uniform morphology and size on the surface of TiO_2, which should be a more optimal choice to achieve the best photocatalytic performance. Here, a hybrid architecture comprising CeF_3 nano-disks dispersed on TiO_2 nano-sheet film () was fabricated using a facile one-step microwave-hydrothermal synthesis. The underlying growth mechanism was discussed. The interesting CeF_3/TiO_2 hybrid system exhibit excellent upconversion luminescence properties and photocatalytic activities for the degradation of MB. Finally, a photodegradation mechanism was proposed as well.

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[*] Corresponding author.
E-mail address: fanjun@nwu.edu.cn (J. Fan).
[1] Jun Wan and Lin Sun are co-first authors; they contributed equally to the work.

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2. Experimental

The detailed materials preparation and characterizations are available in ESI.

3. Results and discussion

The morphologies of the samples were investigated by SEM and TEM. The overall appearance of the TiO_2 NSF is shown in Fig. 1(a), which consists of a large number of continuous distributed nanosheet films. It has a large surface area to provide more active sites for photoreaction. And the nanosheet film structure is regard as a wonderful substrate for the growth of UC materials [7]. Fig. 1(b) and (e) showed the typical SEM and TEM images of the as-prepared CeF_3, it can be seen that the CeF_3 exhibit fascinating chain structures which built from many nanodisks in a particular way of layer-by-layer. As the assembled unit, the mean thickness and diameter of the nanodisks are measured to be about 70 nm and 190 nm. Fig. 1(f) gives a magnified cross-section view of the nanodisks, the side surface of CeF_3 is not smooth, which indicates that the nanodisks have a hierarchical architectures. Besides, the nanodisks assemble together into aggregates in a way of surface-to-surface contact. The HRTEM image (Fig. 1(g)) of the nanodisk (shown in Fig. 1(f)) makes clear that it is a single crystal and the fringe spacing is about 3.25 Å, which corresponds to the crystal spacing of the (111) lattice plane in the CeF3 crystals. Fig. 1(c) and (d) illustrates the morphology of CeF_3 deposited TiO_2 NSF. It is apparent that the CeF_3 nano-disks are in-situ synthesized on the surfaces of TiO_2 nanosheet film. The CeF_3 nanodisks are separated independently in the hybrid system, which indicate that the composite of CeF_3 and TiO_2 restrain the self-assembled process of CeF_3. Besides, there is no barrier between the CeF_3 nanodisks and TiO_2 NSF by the direct surface-to-surface contact, greatly facilitating the energy transfer between the two materials.

Fig. 1(h) gives XRD patterns of the CeF_3, TiO_2 NSF and CeF_3/TiO_2 NSF. All the diffraction peaks of the samples are in good agreement with those of the hexagonal phase CeF_3 (JCPDS no. 08-0045) and anatase TiO_2 (JCPDS no. 21-1272). The CeF_3/TiO_2 NSF composite exhibits distinct diffraction peaks corresponding to CeF_3 and TiO_2, reflecting a two-phase composition in the composite. These narrow and strong diffraction peaks of the samples suggest that the CeF_3 nanodisks and TiO_2 NSF is highly crystallized. According to the analysis above, the corresponding synthesis strategy is schematically depicted in Fig. 2.

The UV–vis diffuse reflectance spectra of the samples are shown in Fig. 3(a). It can be seen that CeF_3 exhibits a relatively weak absorption in the whole region. However, TiO_2 NSF exhibits good absorbance in the ultraviolet and visible light region, which indicates that the unique nano-sheet films structure of TiO_2 is good for light harvest. Stronger absorption can be observed both in the UV–vis light regions for the CeF_3/TiO_2 NSF composite compared to pure TiO_2, indicating that the synthesis of CeF_3/TiO_2 hybrid system favor better light absorption. Additional UV–vis DRS of other CeF_3/TiO_2 composites with different CeF_3 contents are also recorded and are shown in Fig. 3(a). It can be found that 0.03 M CeF_3/TiO_2 NSF exhibits the highest absorption intensity compared to other CeF_3/TiO_2 composites.

UC photoluminescent spectra of the CeF_3 are shown in Fig. 3(b). Under 525 nm visible light excitation, a strong peak appear in the UV region center at 325 nm, which can be assigned to the 5D $\rightarrow {}^2F_{7/2}$ transitions of Ce^{3+} ions. In addition, a relative weak UV emission peak at 325 nm can be also found under the excitation wavelength of 554 nm, 781 nm and 852 nm (Fig. S1). The phenomenon demonstrates that the upconversion is dominated by a two-photon excitation process of visible light and a three-photon excitation process of NIR light [17]. After combining with TiO_2 NSF, one can find that the UV emissions from the CeF_3 nanodisks decreased evidently, suggesting that most UV emissions have been absorbed by the TiO_2 NSF, which will improve the photocatalytic performance under visible irradiation.

The photocatalytic performance of the samples were evaluated by degradation of methylene blue (MB) under different irradiation bands of a Xe lamp (Fig. 3(c)), the details of the photocatalytic activity measurement were shown in the ESI. The C/C_0 conversion plots for MB degradation showed that MB was very stable in the

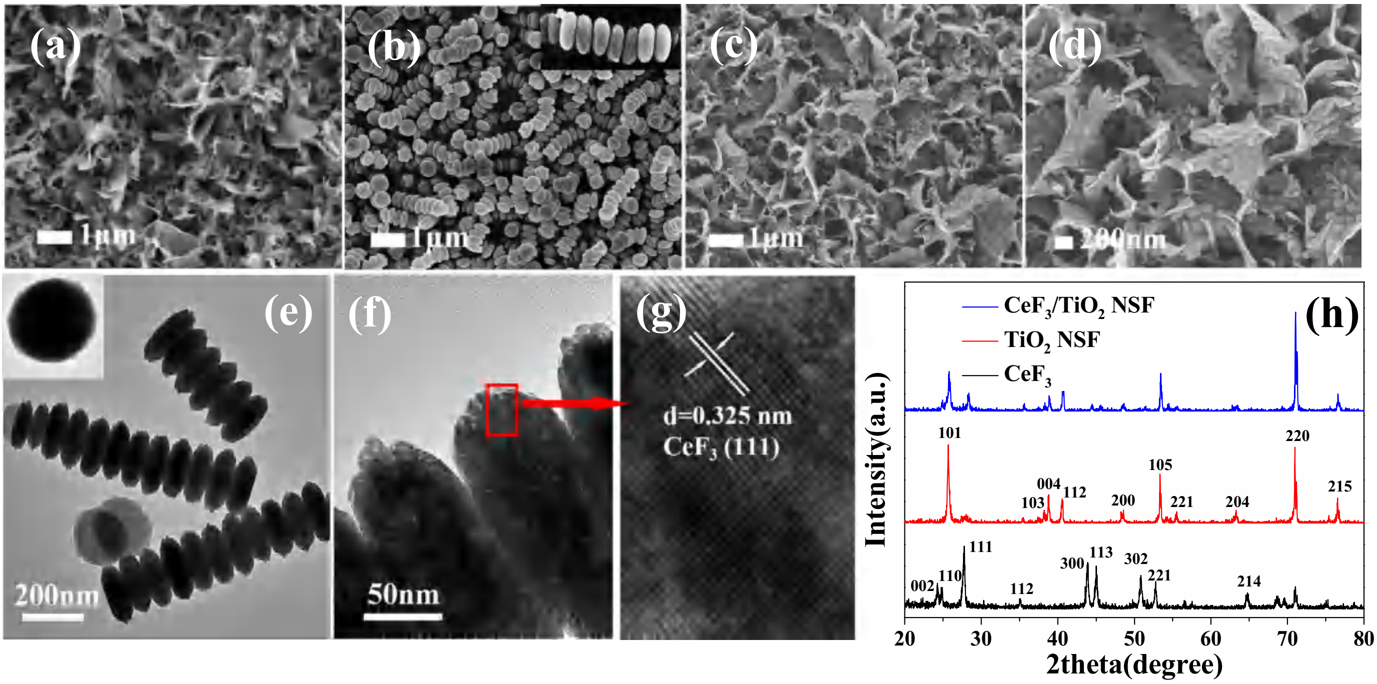

Fig. 1. SEM images of prepared samples: (a) TiO_2 NSF, (b) self-assembled CeF_3 nano-disks, (c) and (d) CeF_3/TiO_2 NSF hybrid system; (e) and (f) TEM image of the CeF_3 nano-disks, (g) HRTEM image of the nano-disk; (h) XRD patterns of the samples.

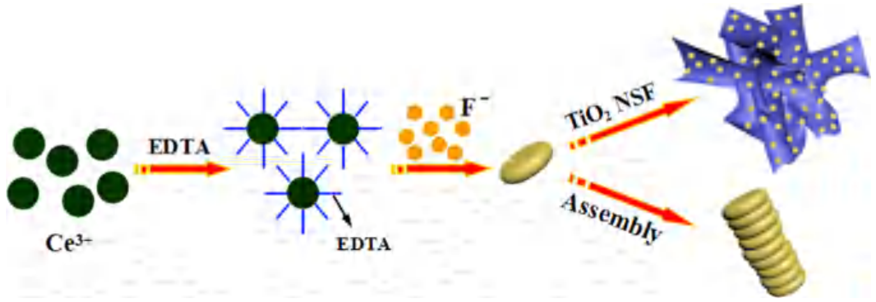

Fig. 2. Schematic illustration of the synthetic procedure for the preparation of CeF_3 nano-disks and CeF_3/TiO_2 NSF hybrid.

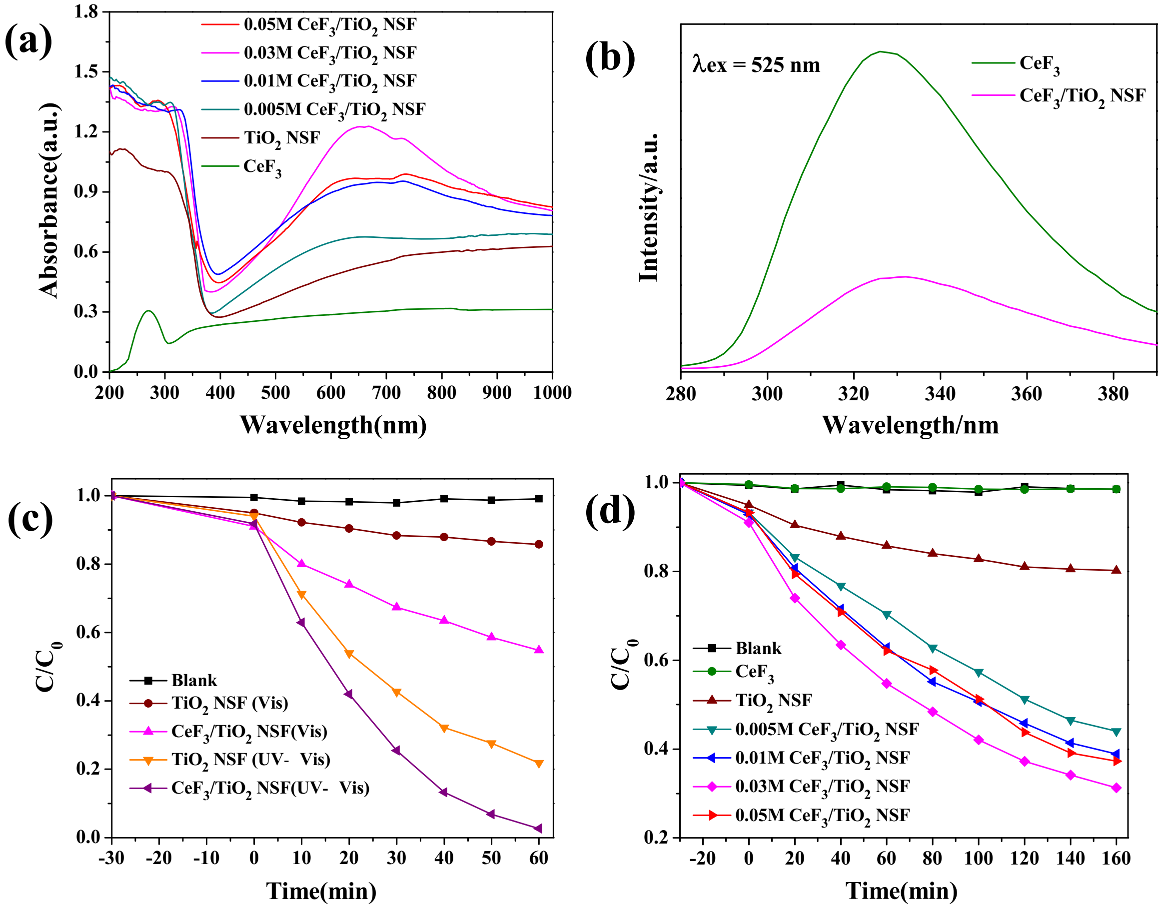

Fig. 3. (a) UV–vis diffuse reflectance spectra of the samples; (b) upconversion luminescence spectra of CeF_3 and CeF_3/TiO_2 NSF; (c) comparison of photocatalytic activities of CeF_3 and CeF_3/TiO_2 NSF under different irradiation bands; (d) photocatalytic degradation of MB as a function of irradiation time for different samples under visible light.

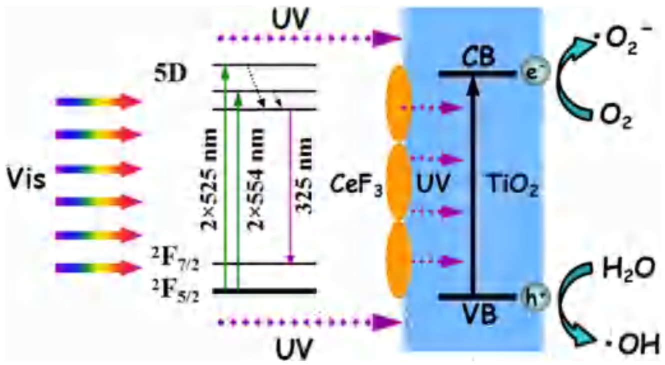

Fig. 4. The proposed photocatalytic mechanism of the CeF_3/TiO_2 NSF hybrid materials.

absence of photocatalysts. When the CeF_3/TiO_2 NSF was irradiation under visible light, a notable decrease in MB concentration was observed within 60 min, while the TiO_2 NSF has no obvious catalytic activity in the visible light region. This result implies that the CeF_3/TiO_2 NSF can serve as visible-driven photocatalysts, the better performance of CeF_3/TiO_2 NSF composite should be attributed to the upconversion fluorescence properties of CeF_3. At the same time, a much faster degradation of MB solution by CeF_3/TiO_2 NSF can be realized under the UV–vis light irradiation compared to the pure TiO_2 system. The photocatalytic mechanism of the prepared CeF_3/TiO_2 NSF under the UV–vis light shown in Fig. 4. The TiO_2 NSF can directly excited by UV light and produce electron–hole pairs to activate photocatalytic reactions. When the hybrid system are exposed under visible light, the CeF_3 nanodisks can serve as a light transducer, which could upconvert two visible photons to be a UV photon, and the upconversion emissions of UV light will be directly harvested by TiO_2 NSF. The excited electron–hole pairs will generate reactive species ($\bullet O_2^-$ and $\bullet OH$) in solution for the photocatalytic oxidation. As a result, the CeF_3/TiO_2 NSF composite exhibits an excellent UV–vis light photocatalytic activity by increasing the utilization of light.

To further investigate the influence of CeF_3 on photocatalytic performance of CeF_3/TiO_2 NSF, additional experiments were carried out under visible light irradiation (Fig. 3(d)). It could be found that the degradation of MB by CeF_3 nanodisks is negligible, but the MB solution can be slight decomposed by pure TiO_2 attributed to large surface area and good light harvest capability, which will promote the self-degradation of MB solution. The CeF_3/TiO_2 NSF samples show a significantly stronger catalytic efficiency than that of CeF_3 and TiO_2. These results further confirm that the UCM of CeF_3 is the critical factor for the high photocatalytic activity of hybrid system where more visible light energy could be used. Moreover, it is clearly seen that the degradation efficiency of MB are affected by CeF_3 concentrations in the samples. The 0.03M CeF_3/TiO_2 NSF heterostructure exhibits the highest photocatalytic activity among these catalysts, the overload of CeF_3 will decrease the light absorption by TiO_2 NSF and reduce energy transfer from the CeF_3 to the TiO_2. As a consequence, the appropriate loading CeF_3 on the surface of TiO_2 NSF is beneficial to the photocatalytic performance due to the UC fluorescence of CeF_3.

4. Conclusion

In summary, a novel UV–vis photocatalyst of CeF_3/TiO_2 NSF with upconversion properties was synthesized via a facile one-step microwave-hydrothermal synthesis. As the upconversion photocatalyst, these hybrid materials can work under both UV and vis bands, and show excellent photocatalytic activities for MB degradation and strong upconversion fluorescence of CeF_3. The effect of CeF_3 concentration on their photocatalytic activities also has been discussed. This strategy may also be applied in design and fabrication of other photocatalysts to improve light utilization of solar energy.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2016.01.069.

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