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Obvious effect of molybdenum supporting on morphology and upconversion luminescence of Er-Yb:TiO₂ and improvement of H_2 generation for $W_{18}O_{49}$



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ABSTRACT

A fascinating strategy of molybdenum ions supporting was utilized to enhance green upconversion (UC) emissions of Er-Yb:TiO₂ prepared by sol-gel method. Er-Yb:TiO₂ nanoparticles exhibited irregular sizes approximately 100–350 nm, which showed stronger red emission and weaker green emissions under the irradiation of near-infrared (NIR). After molybdenum ions supporting, Er-Yb:TiO₂ nanoparticles were turned into uniformly dispersed eight prism structure and average particle size reached about 800 nm. Also, the green UC luminescence integrated intensity of Mo/Er-Yb:TiO₂ was about 46 times improved than that of Er-Yb:TiO₂. Furthermore, a novel photocatalyst of Mo/Er-Yb:TiO₂@W₁₈O₄₉ quasi-core/shell heterostructure was designed based on the localized surface plasmon resonances (LSPR) effect of W₁₈O₄₉ through solvothermal process. With the excitation of NIR, the photocatalytic property of Mo/Er-Yb:TiO₂@W₁₈O₄₉ for H₂ producing from ammonia borane (BH₃NH₃) was researched. H₂ production was about 2-fold enhancement compared with that of W₁₈O₄₉. Besides, the application of natural sunlight for H₂ producing was provided. About 3 times H₂ yield was obtained in contrast to that of W₁₈O₄₉. This work provided an effective way to enhance UC luminescence intensity and H₂ production efficiency for solving energy deficiency problems.

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1. Introduction

RE ions doped UC luminescence materials attracted much attention due to applications of color display, sensor technology, vivo imaging and etc [1]. In the traditional Er^{3+} doped materials, Yb^{3+} was always employed as sensitizer, which could enhance the emission intensity through energy transfer (ET) by virtue of large absorption cross-section at 980 nm and similar energy level structure with Er^{3+} [2]. Studies revealed that the selection of host materials was crucial factor, simultaneously. RE-fluoride was considered as a promising material owing to lower photon energy [3–6]. Compared to the former, RE-oxide materials possessed numerous merits such as favourable thermal stability, chemical stability and simple preparation processes [7]. Nonetheless,

disadvantage like higher phonon energy also existed, which failed to prevent non-radiative relaxation. Poor luminescence efficiency was still bottleneck problem within the UC luminescence system [3,8-10]. In order to overcome the difficulties, we developed a new tactic that Er-Yb:TiO₂ was supported with molybdenum ions, which exhibited remarkably improved UC luminescence properties comparing with conventional Er-Yb system.

LSPR effect was widely investigated in noble metal nanoparticles [11–14], which could be utilized to enhance fluorescence intensity [15], photocatalytic activities [11,16] and etc. However, the disadvantage of high cost still limited the practical application. In recent years, some semiconductors such as WO_{3-x} , $Cu_{2-x}S$ and MOO_{3-x} were also proved to possess LSPR effect [17–20]. Among these, low-cost $W_{18}O_{49}$ nanowires structure [21] was one of the most satisfying candidate material triggering researchers' interest attributed to the fact that it equipped a mass of exterior free electrons originated from plentiful oxygen defects, whose LSPR absorption stretched across visible and the whole NIR region [17,22]. Upon the excitation of visible and NIR, strong LSPR effect could be





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driven, thereby generating "hot electrons" [23–26], which might be the key to reducing hydrogen ions from BH₃NH₃ for H₂ evolution. Taking advantage of sunlight as excitation source for photocatalytic H₂ production further explored a prospective method for solving contemporary energy shortage problems. As a consequence, it was meaningful to design a quasi-core/shell structures [27] to employ UC emissions for photocatalysis, availably.

Here, we reported an efficient technique for improving UC luminescence ability of Er-Yb:TiO₂ by molybdenum ions supporting. The morphology of Mo/Er-Yb:TiO₂ was changed into regular eight prism structure controllably from original amorphous morphology. The broad absorption band in the NIR and visible regions attributed to the abundant oxygen vacancies of $W_{18}O_{49}$ that grown on the surface of Mo/Er-Yb:TiO₂ and robust LSPR effect contributed to H₂ evolution by hydrolyzing BH₃NH₃ under UC luminescence and natural sunlight functions.

2. Experimental section

2.1. Synthesis of the Er-Yb:TiO₂

The Er-Yb:TiO₂ were prepared via sol-gel process. The iso-propyl (i-PrOH) was poured slowly into the mixture of n-butyl titanate (Ti(OBu)₄), acetylacetone (AcAc) and deionized water under continuous agitation by magnetic stirrer for 1 h to form the precursor. HNO₃ was introduced into precursor solution to adjust the PH value to about 3.0. The mixture was stirred for 6 h, forming transparent sols. The molar ratios of Ti(OBu)₄ to AcAc, H₂O and HNO₃ were 1:1, 1:2 and 3:1, respectively. The Er(NO₃)₃·6H₂O and Yb(NO₃)₃·6H₂O were added in the sol with molar ratios 1:5:100 for Er³⁺: Yb³⁺: Ti⁴⁺. Then the sols dissolved with RE were dried at 373 K for 6 h to obtain xerogels. Finally, xerogels were calcinated at 1273 K with the heating rate of 4 K/min for 1 h and cooled down to room temperature. The obtained products of Er-Yb:TiO₂ were milled into powders for structure analysis and spectral measurement.

2.2. Synthesis of Mo/Er-Yb:TiO₂

The Mo/Er-Yb:TiO₂ were synthesized by impregnation supporting method. Firstly, 0.2 mol/L of $(NH_4)_6Mo_7O_{24}$ ·4H₂O aqueous solution was added into a crucible loaded with 0.2 g of Er-Yb:TiO₂. Stirring the mixture successively until the formation of uniform suspension. Next, the suspension was dried to get rid of solvent and calcinated at 1273 K with the heating rate of 4 K/min to gain the Mo/Er-Yb:TiO₂.

2.3. Fabrication of Mo/Er-Yb:TiO₂@W₁₈O₄₉

The Mo/Er-Yb:TiO₂@W₁₈O₄₉ were prepared through solvothermal approach. In a typical procedure, 2 mg of Mo/Er-Yb:TiO₂ were added into 20 mL of alcohol dissolved with 25 mg of W(CO)₆ entirely. After that, the mixture was transferred into Teflon-lined autoclave and reacted for 12 h at 433 K, then the Mo/Er-Yb:TiO₂@W₁₈O₄₉ were fabricated.

2.4. Preparation of Mo/Er-Yb:TiO₂@WO₃

As prepared Mo/Er-Yb:TiO₂@ $W_{18}O_{49}$ was put into crucible and placed in furnace, annealing for 2 h at 737 K to gain Mo/Er-Yb:TiO₂@ WO_3 .

2.5. H₂ evolution experiments

Deionized water was added into a quartz reactor loaded with 2 mg of Mo/Er-Yb:TiO₂@W₁₈O₄₉. Sealing it with rubber plug and

sealant closely. Then injecting argon gas to exhaust the residual air for 15 min and adding 0.8 mL of BH₃NH₃ aqueous solution by syringe. The reaction vessel was fixed on a magnetic stirrer and irradiated by 980 nm fiber laser continually for 1 h. The generated gas was collected every 15 min. The experiments were under the condition of ice bath to prevent the thermal energy produced from $W_{18}O_{49}$ impacting the experimental accuracy (Thermal decomposition of BH₃NH₃ could generate H₂). In addition, taking advantage of focused sunlight as excitation source for catalysis H₂ evolution was executed through the above methods. The measure of $W_{18}O_{49}$ and BH₃NH₃ for H₂ evolution effect as check experiments were performed, simultaneously.

2.6. Materials characterization

Samples were characterized for their surface morphology, crystal structures, UC luminescence spectra and photocatalysis H₂ producing capacity. X-ray diffraction measurements were analyzed by SHIMADZU XRD-6000 X-ray diffractometer (XRD) with Cu-Ka radiation. Diffraction patterns were recorded in the 2θ range of 10°-80° with scan speed of 2°/min. Surface morphology, crystallite size and elements analysis were performed using HITACHI S-4800 field emission scanning electron microscope (SEM) with energy dispersive spectrometer (EDS). UC luminescence spectra were conducted by Olympus Microscope DP80 and Jobin-Yvon iHr550 monochromator detected with CR131 photomultiplier tube associated with a lock-in amplifier. The resolution of spectrum was set to 0.2 nm. The absorbance spectra were measured by PerkinElmer Lambda 750 UV/VIS/NIR Spectrometer. Gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) (Beifen-Ruili Analytical Instrument, SP-3420A) was utilized for the H₂ producing properties measurement.

3. Results and discussion

3.1. Morphology and structure characterization

As observed from SEM images, Er-Yb:TiO₂ presented irregular shape (Fig. 1 (a)) while Mo/Er-Yb:TiO₂ suggested well-distributed eight prism architecture, particles size was approximately 800 nm (Fig. 1 (b)). With the increase of volume for molybdenum ions supporting, the structure of Mo/Er-Yb:TiO₂ tended to randomization (Fig. S1, Supporting Information). Mo/Er-Yb:TiO₂@W₁₈O₄₉ and Mo/Er-Yb:TiO2@WO3 showed rod-like structures based on the prism morphology of Mo/Er-Yb:TiO₂ with favourable dispersity (Fig. 1 (c, d, e and f)). XRD profiles revealed in Fig. 2A (a) that the Er-Yb:TiO₂ was rutile phase (JCPDS 21-1276). The diffraction pattern did not suggest the presence of RE oxide, which demonstrated that RE ions were doped in the TiO₂, completely. Mo/Er-Yb:TiO₂ indicated that the main phase was also rutile TiO₂, the diffraction peaks of Yb₂(MoO₄)₃ (JCPDS 33-1451) appeared, synchronously (Fig. 2A (b)). And Fig. 2A (c) suggested the major feature diffraction peaks of Mo/Er-Yb:TiO₂ and W₁₈O₄₉, which could be indexed as monoclinic phase (JCPDS 71-2450). After calcination for 2 h, W₁₈O₄₉ was oxidized and turned into WO₃, which was in conformity with JCPDS card 71-1310 (Fig. 2A (d)). EDS analysis implied that Mo/Er-Yb:TiO2@W18O49 quasi-core/shell heterostructure consisted of multi elements including C, O, W, Mo, Yb and Ti. It is a strong possibility that the appearance of C element resulted from organic groups, which was due to the solvothermal process for preparing Mo/Er-Yb:TiO2@W18O49 (Fig. 2B). The joint certification of XRD and EDS indicated that W18O49 was fabricated on the surface of Mo/Er-Yb:TiO₂, successfully.



Fig. 1. SEM analysis of as-prepared samples: (a) Er-Yb:TiO₂; (b) regular eight prism morphology of Mo/Er-Yb:TiO₂; (c, d) rod-like structure of Mo/Er-Yb:TiO₂@W₁₈O₄₉; (e, f) Mo/Er-Yb:TiO₂@WO₃.



Fig. 2. (A) XRD patterns of (a) Er-Yb:TiO₂, (b) Mo/Er-Yb:TiO₂, (c) Mo/Er-Yb:TiO₂@W₁₈O₄₉ and (d) Mo/Er-Yb:TiO₂@WO₃; (B) EDS plot of Mo/Er-Yb:TiO₂@W₁₈O₄₉ quasi-core/shell heterostructure.

3.2. UC luminescence characterization

UC luminescence spectra, shown in Fig. 3 (A), was the Er-Yb:TiO₂ and Mo/Er-Yb:TiO₂ measured in the same condition with Olympus Microscope DP80 under 980 nm laser excitation. The Er-Yb:TiO₂ emerged higher red UC emission peak corresponding to ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ transition while strong green UC luminescence could be

detected in Mo/Er-Yb:TiO₂ originating from the transitions of ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$. In Er-Yb system, Er³⁺ obtained energy from Yb³⁺ via ET to populate on level ${}^{4}I_{11/2}$. The probability of Er³⁺ nonradiative relaxation ${}^{4}I_{11/2} \rightarrow {}^{4}I_{13/2}$ was greater than that of ${}^{4}I_{11/2} \rightarrow {}^{4}F_{7/2}$, which resulted from intense lattice phonon couplings of oxide matrix material. And the transition ${}^{4}I_{13/2} \rightarrow {}^{4}F_{9/2}$ performed a main role through ET and excited state absorption (ESA),



Fig. 3. (A) The UC luminescence spectra of Er-Yb:TiO₂ and Mo/Er-Yb:TiO₂, insets showed the micro-area optical images under the Olympus Microscope and enhancement factor of UC luminescence after molybdenum ions supporting. (B) Photon fitting curves: green emissions of Mo/Er-Yb:TiO₂; red emission of Er-Yb:TiO₂; green emissions of the references to color in this figure legend, the reader is referred to the Web version of this article.)

which resulted in stronger red UC emission. The supporting of molybdenum ions led to the peak of green emissions from ${}^{2}H_{11/}$ $_2 \rightarrow {}^4I_{15/2}$ transition split obviously and the green UC luminescence intensity was enhanced considerably. The intensity of green UC emissions was monotonic increasing with the enhancement of load for molybdenum ions. (Fig. S2, Supporting Information). However, the band of red emission hardly changed but intensity. The formation of $Yb_2(MoO_4)_3$ with lower lattice vibration energy by virtue of heavy metal elements Yb and Mo could prevent nonradiative transitions between energy levels within RE ions [28,29]. Low lattice symmetry was also advantageous to enhance crystal field, thereby providing a lower threshold of excitation. Meanwhile, it is crucial factor that larger proportion of rare earth ions was contained in Yb₂(MoO₄)₃. Besides, weaker red emission might be derived from energy level characteristics for MoO_{a}^{2-} . As a result, integrated intensity of green emissions for Mo/Er-Yb:TiO₂ was improved extraordinarily by a factor of about 46 and lowered that of red emission to almost 1/10 for the Er-Yb:TiO₂. Fig. 3 (B) proved the excitation power dependence of ${}^{2}H_{11/2}$, ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}F_{9/2}$ $_2 \rightarrow {}^4I_{15/2}$ transitions of Mo/Er-Yb:TiO₂ and Er-Yb:TiO₂, severally. It was clear that photons were required to populate the upper emitting states for unsaturated UC processes [30], the UC emission intensity I_{up} is proportional to the nth power of the pump power P_{pump}, which can be expressed as

$I_{up} \propto P_{pump}^n$

Iup and n were UC emission intensity and the number of photons

required to populate the green and red UC emission states, respectively. The slopes of the fitting curves in the Ln-Ln plots were less than 2.1 and greater than 1.6, which demonstrated that two-photon processes were responsible for the UC luminescence of Er-Yb:TiO₂ and Mo/Er-Yb:TiO₂.

To illustrate the influence of LSPR from $W_{18}O_{49}$ on UC luminescence, the emission spectra of Mo/Er-Yb:TiO₂@W₁₈O₄₉ and Mo/Er-Yb:TiO₂@WO₃ were tested. Most of UC emissions from Mo/Er-Yb:TiO₂@WO₃ were tested due to intense LSPR of $W_{18}O_{49}$ shell (Fig. 4 A), which enabled that Mo/Er-Yb:TiO₂@W₁₈O₄₉ indicated faint UC emissions (Fig. 4 B). After annealing, oxygen vacancies of $W_{18}O_{49}$ was passivated at air atmosphere and generated WO₃, which revealed eliminated LSPR absorption and led to boost green luminescence for Mo/Er-Yb:TiO₂@WO₃. Meanwhile, the positive effect of LSPR for UC luminescence from $W_{18}O_{49}$ has been provided in supporting information (Fig. S3, Fig. S4).

3.3. H₂ evolution

Fig. 5 (A) showed H₂ production over different samples versus the time. Mo/Er-Yb:TiO₂@W₁₈O₄₉ and W₁₈O₄₉ possessed more efficient photocatalytic activity for H₂ evolution, whose H₂ yield were 1.79 and 0.89 µmol, respectively. The BH₃NH₃ exhibited extremely low H₂ producing efficiency, which far less than that of Mo/Er-Yb:TiO₂@W₁₈O₄₉ and W₁₈O₄₉. It indicated that LSPR effect of W₁₈O₄₉ nanowires played a significant role while BH₃NH₃ was slowly hydrolyzed without photocatalyst in H₂ evolution processes.



Fig. 4. (A) The absorption spectra of W₁₈O₄₉ (dark) and WO₃ (light), insets showed the color comparision between above samples; (B) emission spectra of Mo/Er-Yb:TiO₂@WO₃ and Mo/Er-Yb:TiO₂@WO₃ under excitation of 980 nm, insets supplied the micro-area optical images under the Olympus Microscope. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 5. (A) H₂ evolution for Mo/Er-Yb:TiO₂@W₁₈O₄₉, W₁₈O₄₉ and BH₃NH₃ upon the excitation of 980 nm laser; (B) the normalized absorbance spectrum of W₁₈O₄₉, inset revealed the UC luminescence of Mo/Er-Yb:TiO₂.



Fig. 6. (A) H₂ production for Mo/Er-Yb:TiO₂@W₁₈O₄₉, W₁₈O₄₉ and BH₃NH₃ under the irradiation of natural sunlight; (B) the schematic diagram of H₂ evolution for Mo/Er-Yb:TiO₂@W₁₈O₄₉ quasi-core/shell heterostructure.

The absorption spectrum of W₁₈O₄₉ corresponding to the emission spectrum of Mo/Er-Yb:TiO₂ was shown in Fig. 5 (B). Strong LSPR absorption spanning from visible region to NIR proved the LSPR effect could be driven by green UC luminescence of Mo/Er-Yb:TiO2 and NIR, forcefully. Under the motivation of NIR, the resonance of exterior electrons that originated from abundant oxygen vacancies of W₁₈O₄₉ was caused, resulting in the LSPR effect, which enhanced incident light and excited the UC luminescence from Mo/Er-Yb:TiO2. The UC emissions would be absorbed, which re-excited the LSPR effect of W₁₈O₄₉, leading to the formation of "hot electrons", which was in favor of combining the hydrions resulted from hydrolyzed BH₃NH₃ for producing H₂. Therefore, the highest yield of H₂ for Mo/Er-Yb:TiO₂@W₁₈O₄₉ was consistent with the description in Fig. 5 (A), which was about 2 times than that of $W_{18}O_{49}$. The icebath condition reduced photoinduced heat from W₁₈O₄₉ under the irradiation of 980 nm laser, suppressing the fluence derived from thermal decomposition of BH₃NH₃ for generating H₂ and further confirming the contribution of UC emissions for H₂ evolution.

In order to prove the practical application of Mo/Er-Yb:TiO₂@W₁₈O₄₉ quasi-core/shell heterostructure for photocatalytic H₂ producing, natural sunlight focused by magnifying glass was used as excitation source. At the excitation of 550 mW/ cm² sunlight, other than the influence of UC emissions, photothermal effect from W₁₈O₄₉ also became substantial factor impacting the H₂ production. Broadband absorption ensured large spectral response range and utilization ratio of sunlight. UC luminescence promoted LSPR and generation of "hot electrons". As offered in Fig. 6 (A, B), BH₃NH₃ still exhibited inefficiency on H₂ evolution and the H₂ production of Mo/Er-Yb:TiO₂@W₁₈O₄₉ was 3.3 times higher than that of W₁₈O₄₉, which demonstrated that Mo/Er-Yb:TiO₂@W₁₈O₄₉ quasi-core/shell heterostructure could act as superior photocatalyst to promote H₂ producing efficiency.

In summary, we investigated the UC emission spectra of Er-Yb:TiO₂, Mo/Er-Yb:TiO₂, Mo/Er-Yb:TiO₂@W₁₈O₄₉ and Mo/Er-Yb:TiO₂@WO₃ upon the excitation of 980 nm fiber laser under Olympus Microscope DP80. In the eight prism shaped Mo/Er-Yb:TiO₂ system, the formation of Yb₂(MoO₄)₃ became indispensable factors, which considerably enhanced the green UC luminescence intensity and quenched the red emission. The conclusion of two photon processes for Er-Yb:TiO₂ and Mo/Er-Yb:TiO₂ was drawn. Mo/Er-Yb:TiO₂@WO₃ represented more intense UC luminescence than Mo/Er-Yb:TiO₂@WO₁₈O₄₉ because of the absorption effect of W₁₈O₄₉. W₁₈O₄₉ nanowires were fabricated on the surface of Mo/Er-Yb:TiO₂, whose LSPR effect could be excited by NIR and reexcited by the action of UC emissions from Mo/Er-Yb:TiO₂, which was conductive to form "hot electrons" and hydrolyzing BH₃NH₃ for

 H_2 producing under NIR excitation, subsequently. Finally, the examination of H_2 evolution upon sunlight excitation illustrated Mo/ Er-Yb:TiO₂@W₁₈O₄₉ possessed potential practical application. Accordingly, this work would provide a high-efficiency strategy to enhance UC luminescence intensity and superinduce a prospective technique of utilizing UC emissions to catalyze for H_2 evolution and tackle energy deficiency issues.

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Appendix A. Supplementary data

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