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Article

TiO₂ composite nanotubes embedded with CdS and upconversion nanoparticles for near infrared light driven photocatalysis

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ABSTRACT

We report a colloidal process to coat a layer of TiO₂ onto SiO₂ composite nanofibers containing embedded CdS and upconversion nanoparticles (UCNPs). The SiO₂ composite nanofibers were fabricated by electrospinning. To improve the energy transfer efficiency, UCNPs and CdS nanoparticles were bound in close proximity to each other within the SiO₂ matrix. β-NaYF₄:Yb(30%),Tm(0.5%)@NaYF₄:Yb(20%),Er(2%) core-shell nanoparticles were used as nanotransducers for near infrared light. These nanoparticles exhibited enhanced upconversion fluorescence compared with β-NaYF₄:Yb(30%),Tm(0.5%) or β-NaYF₄:Yb(30%),Tm(0.5%)@NaYF₄ nanoparticles. The morphologies, size and chemical compositions have been extensively investigated using field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS), respectively. The TEM images showed that the TiO₂ composite nanotubes were embedded with a large amount of UCNPs and CdS nanoparticles. The composite TiO₂ nanotubes degraded more than 90% of rhodamine B (RhB) dye during 20 min of irradiation by simulated solar light. In particular, more than 50% of RhB was decomposed in 70 min, under irradiation of near infrared light (NIR). This high degradation was attributed to the full spectrum absorption of solar light, and the enhanced transfer efficiency for near infrared light. The as-prepared nanostructures can harness solar energy, and provide an alternative to overcome energy shortages and environmental protection.

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1. Introduction

Composite nanostructures with enhanced physical and chemical properties have gained scientific and technological interest due to their applications in photocatalysis [1–4], opto-

electronic devices [5,6], solar cells [7–10], and drug delivery [11–13]. In the past two decades, much effort has been made to develop techniques for fabricating nanocomposites with well controlled sizes and morphologies. These have included calcination [14], co-precipitation [15–17], epitaxial growth [18–20],

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self-assembly [21–28], electrospinning [29–31], sol-gel [32] and hydrothermal [33,34] methods. In particular, electrospinning has been recognized as an efficient, low cost and versatile method for synthesizing composite nanofibers including Au/PVP [35], TiO_2 /polyvinyl pyrrolidone (PVP) [36], graphene oxide/PVA [37], Ag/multi-wall nanotubes/polyacrylonitrile (PAN) [38], upconversion nanoparticles (UCNPs)@ SiO_2 [32], and SnO_2 @ TiO_2 [39]. Lanthanide ion-doped upconversion phosphors have been widely used as efficient nanotransducers. They can transform near infrared (NIR) photons to high energy photons with ultraviolet-visible (UV-Vis) wavelengths. This has led to their application in solid state lasers, solar cells, flat-panel displays, bioimaging, chemotherapy, and photodynamic therapy [40–48]. Nanocomposites incorporated with UCNPs including UCNPs/CdSe [49,50], UCNPs/CdTe [51,52], UCNPs/CdS [53], UCNPs/ TiO_2 [54–61], and UCNPs/reduced graphene oxide [62] have been prepared and used for optimizing solar absorption. We recently demonstrated a facile process to fabricate UCNPs/CdS/ TiO_2 nanofibers, which enabled full solar spectrum absorption for enhanced photocatalysis [63]. However, the distance between the UCNP and CdS chromophores was difficult to control, which reduced the energy transfer efficiency. CdS can be excited by photons from the excited state levels including $^1\text{I}_6 \rightarrow ^3\text{F}_4$, $^1\text{D}_2 \rightarrow ^3\text{F}_4$, $^1\text{D}_2 \rightarrow ^3\text{H}_6$, and $^1\text{G}_4 \rightarrow ^3\text{H}_6$ of Tm^{3+} for $\text{NaYF}_4\text{:Yb/Tm}$ nanoparticles [53,63]. The excited state levels ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$) of Er^{3+} can also excite CdS, according to the proposed energy transfer process in Fig. 1. The fluorescence energy transfer efficiency will also be enhanced if $\text{NaYF}_4\text{:Yb/Tm}$ or $\text{NaYF}_4\text{:Yb/Tm@NaYF}_4$ nanoparticles are replaced by $\text{NaYF}_4\text{:Yb/Tm@NaYF}_4\text{:Yb/Er}$ nanoparticles. The distance between the UCNP and CdS or TiO_2 chromophores can significantly affect the fluorescence energy transfer efficiency [64].

In the current study, we used an electrospinning process to combine $\text{NaYF}_4\text{:Yb/Tm@NaYF}_4\text{:Yb/Er}$ and CdS nanoparticles in close proximity in a SiO_2 matrix. We first prepared UCNPs/ethyl silicate (TEOS)/CdS/PVP nanofibers and UCNPs/ SiO_2 /CdS/PVP nanofibers by electrospinning, accord-

ing to our modified protocol [63,65]. A sol-gel process was then used to coat a layer of TiO_2 on the UCNPs/ SiO_2 /CdS/PVP nanofibers, and subsequent calcination at 500 °C for 2 h yielded TiO_2 composite nanotubes embedded with UCNPs and CdS nanoparticles. $\text{NaYF}_4\text{:Yb/Tm@NaYF}_4\text{:Yb/Er}$ core-shell nanocrystals (i.e. UCNPs) with enhanced fluorescence emission were prepared as chromophores and nanotransducers. Their fluorescence properties and photocatalytic performance are discussed.

2. Experimental

All chemicals were of analytical grade and used as received without further purification. CdS nanoparticles with an average diameter of 100 nm were synthesized via a hydrothermal method [66]. $\beta\text{-NaYF}_4\text{:Yb(30\%),Tm(0.5\%)@NaYF}_4\text{:Yb(20\%),Er(2\%)}$ core-shell nanoparticles with an average diameter of 40 nm were prepared using a sequential growth process [67].

2.1. Fabrication of UCNPs/TEOS/CdS/PVP nanofibers

The UCNPs/TEOS/CdS/PVP composite nanofibers were fabricated via a modified electrospinning process [63]. In a typical procedure, 0.284 g of PVP was dissolved in 4 mL of absolute ethanol to form a clear solution with vigorous stirring. 0.22 g of as-prepared hydrophilic UCNPs and 0.58 g of CdS nanoparticles were added to the previous solution, which was then ultrasonicated for 10 min. 1.5 mL of TEOS was added and the resulting mixture was stirred vigorously. The mixture was then poured into a 10 mL plastic syringe for electrospinning under a flow rate of 1.1 mL h^{-1} and a voltage of 7 kV. The nanofibers acquired from the collector were UCNPs/TEOS/CdS/PVP nanofibers.

2.2. Synthesis of UCNPs/ SiO_2 /CdS/ TiO_2 composite nanotubes

Before coating the TiO_2 layer on the surface of the UCNPs/CdS/PVP/TEOS nanofibers, the acquired microfibers were calcined in air at 400 °C for 1 h at a heating rate of 1 °C min^{-1} , to prepare UCNPs/ SiO_2 /CdS/PVP nanofibers. In a typical procedure, 0.1 g of UCNPs/ SiO_2 /CdS/PVP nanofibers were dispersed in ethanol (20 mL) under vigorous stirring. 200 μL of TBT and 90 μL of ammonia solution (28–30 wt.%) were added to the above solution. The resulting mixture was stirred at room temperature for 4 h. The product was collected by centrifugation, washed with ethanol three times, and then dried at 50 °C for 8 h. Finally, the as-prepared product was calcined in air at 400 °C for 1 h at a heating rate of 1 °C min^{-1} . This improved the crystallization of the formed titania, and removed the PVP matrix, yielding the UCNPs/ SiO_2 /CdS/ TiO_2 composite nanotubes.

2.3. Characterization

The morphologies of the samples were characterized using field-emission scanning electron microscopy (FESEM) with a SU8020 spectrophotometer (Hitachi, Japan). and transmission electron microscopy (TEM) with a JEM-2100F microscope

Fig. 1. Proposed energy transfer processes between $\text{NaYF}_4\text{:Yb/Tm@NaYF}_4\text{:Yb/Er}$ (UCNPs), CdS, and TiO_2 .

(JEOL, Japan). The crystal phases of the samples were characterized using an X'Pert PRO MPD X-ray diffractometer (PANalytical B.V., Netherlands), using graphite monochromatized Cu K_{α} radiation at 40 kV and 40 mA. X-ray photoelectron spectra (XPS) were recorded on an ESCALab 250Xi X-ray photocatalysts-electron spectrometer (Thermo-VG Scientific, Massachusetts, USA). Fluorescence spectroscopy (Edinburgh FLS980, UK) was used to obtain steady state and dynamic fluorescence spectra of the samples. Absorption spectra were recorded with a CARY 5000 spectrophotometer (Agilent Technologies Inc, California, USA). Total organic carbon (TOC) analysis was carried out using an elemental Liqui II apparatus (Germany).

3. Results and discussion

3.1. Fabrication of UCNPs/TEOS/CdS/PVP nanofibers

Fig. 2a and b show FESEM images of the product obtained from electrospinning 0.284 g of PVP, 0.22 g of hydrophilic UCNPs, 0.58 g of CdS nanoparticles, and 1.5 mL of TEOS. The images show that the product consisted of nanofibers of tens of μm in length and 500 nm in diameter. The nanofibers were decorated or embedded with a high population of nanoparticles, as shown by the TEM images in Fig. 2c and d. The chemical composition of the UCNPs/TEOS/CdS/PVP nanofibers was studied using scanning transmission electron microscopy (STEM) and elemental mapping analysis. Fig. 2e–n show that Si, O, Y, Yb, Er, Tm, Si, Cd, S and Na were detected, confirming their co-existence in the as-obtained nanofibers. The chemical composition was also investigated using energy dispersive X-ray (EDX) analysis, as shown in Fig. 3.

Fig. 2. (a, b) FESEM images of the UCNPs/CdS/PVP/TEOS nanofibers. (c, d) TEM images of the UCNPs/CdS/PVP/TEOS nanofibers. (e) STEM image of a single UCNPs/CdS/PVP/TEOS nanofiber. (f–n) Elemental mapping images of elements in the nanofiber shown in (e). All scale bars are 500 nm.

Fig. 3. EDX spectrum of the UCNPs/CdS/PVP/TEOS nanofibers.

3.2. Fabrication of UCNPs/SiO₂/CdS/TiO₂ composite nanotubes

Fig. 4 shows SEM and TEM images of the final sample, obtained after calcination of the as-prepared UCNPs/CdS/PVP/SiO₂/TiO₂ derived from 0.1 g of UCNPs/SiO₂/CdS/PVP nanofibers (Fig. 5) and 200 μL of TBT in 90 μL of ammonia solution. Fig. 5 shows that the UCNPs and CdS nanoparticles were combined in close contact by the SiO₂ nanoparticles derived from the UCNPs/TEOS/CdS/PVP nanofibers. Fig. 4a and b show that the as-prepared TiO₂ composites were of several hundred nanometers in diameter and tens of μm in length. This was in accordance with the diameter of the electrospun UCNPs/TEOS/CdS/PVP nanofibers. The TEM image in Fig. 4c demonstrated that the obtained product was tube-like and had a shell thickness of 20 nm. The high resolution TEM image in Fig. 4d showed that the shell layer consisted of octahedrite phase of TiO₂ nanoparticles.

X-ray diffraction (XRD) was used to study the crystalline phases and chemical compositions. Fig. 6 shows the XRD pattern of the as-prepared tube-like composite nanofibers of TiO₂. The diffraction peaks at 25.44, 38.02 and 48.12° 2 θ could be indexed to the anatase phase of TiO₂ (JCPDS No. 21-1272), confirming the crystalline TiO₂ shell. Diffraction peaks of the hexagonal phases of CdS (JCPDS No. 41-1049) [68,69] and NaYF₄ (JCPDS No. 28-1192) [47,67] were also clearly observed. These results showed that the as-prepared sample consisted of TiO₂,

Fig. 4. (a, b) SEM images of as-prepared TiO₂ nanotubes embedded with UCNPs and CdS nanoparticles. (c) TEM image of a TiO₂ composite nanotube. (d) High resolution TEM image of the marked region in (c).

Fig. 5. (a) SEM and (b) TEM images of UCNPs/SiO₂/CdS/PVP nanofibers (c) STEM image of a single UCNPs/SiO₂/CdS/PVP composite nanofiber. (d–m) Elemental mapping of Y, Yb, Na, Er, Tm, Si, F, Cd, S and O in composite nanotubes of TiO₂, respectively. All scale bars are 500 nm.

CdS and UCNPs. STEM spectroscopy and XPS were used to characterize the chemical composition and elemental distribution of the as-prepared UCNPs/SiO₂/CdS/TiO₂ composite nanotubes. Fig. 7 shows elemental mapping images for Yb, Y, O, Si, Ti, Tm, S, Na, F, Er and Cd in the composite nanotubes. The images indicated the co-existence of these elements in the UCNPs/SiO₂/CdS/TiO₂ nanotubes. The elemental composition was also investigated by XPS, as shown in Fig. 8. These results collectively indicated that the UCNPs/SiO₂/CdS/TiO₂ nanotubes had been prepared.

3.3. Optical and photocatalytic properties of the

Fig. 6. XRD patterns of the as-prepared UCNPs/SiO₂/CdS/TiO₂ nanotubes, and standard patterns for its various components.

Fig. 7. (a) STEM image of a single nanotube of the UCNPs/SiO₂/CdS/TiO₂ nanocomposite. (b–l) Elemental mapping of Yb, Y, O, Si, Ti, Tm, S, Na, F, Er and Cd in the composite nanotubes of TiO₂, respectively. All scale bars are 500 nm.

UCNPs/SiO₂/CdS/TiO₂ composite nanotubes

The fluorescence spectrum of the as-obtained UCNPs/SiO₂/CdS/TiO₂ composite nanotubes is shown in Fig. 9a. Compared with the spectrum of the UCNPs, the fluorescence emissions of the ¹I₆→³F₄, ¹D₂→³F₄, D₂→³H₆, and ¹G₄→³H₆ transitions of Tm³⁺ and the ²H_{11/2}→⁴I_{15/2} and ⁴S_{3/2}→⁴I_{15/2} transitions of Er³⁺ for the as-prepared TiO₂ composite nanotubes were greatly quenched under excitation by a 980 nm continuous wave (CW) laser. This indicated the enhanced fluorescence energy transfer efficiency of the tube-like UCNPs/SiO₂/CdS/TiO₂ nanostructures. Most of the transitions for Tm³⁺ or Er³⁺ were greatly quenched, which was ascribed to the close proximity of the UCNPs and CdS nanoparticles in the SiO₂ matrix. The near infrared (NIR) photon energy could be efficiently transferred to the nearby CdS nanoparticles via irradiative energy transfer (IET) and non-irradiative energy transfer (i.e. Förster resonance energy transfer (FRET)) processes, as shown in Fig. 1 [63]. Fig. 9b shows the UV-Vis absorption spectrum of the UCNPs/SiO₂/CdS/TiO₂ composite nanotubes. The as-prepared composite nanotubes exhibited full spectrum absorption of solar light, in contrast to the single component CdS or TiO₂. This would improve the photocatalytic performance under NIR or simulated solar irradiation.

As discussed previously, the composite nanotubes contained UCNPs, CdS and TiO₂ nanoparticles in close proximity. This resulted in the full spectrum response to solar light of the nanotubes, as shown in Fig. 9b. The CdS nanoparticles embedded in the composites could be excited by NIR light via FRET from the UCNPs, or directly by visible light from the solar spectrum [53,63]. Scheme 1 shows that excited CdS nanoparticles will produce photo-generated electrons and positive holes. This will result in the formation of reactive oxygen species (ROS) which can decompose organic dyes including Rhodamine B (RhB). Terephthalic acid (TPA) was used as a free radical scavenger, to verify the production of ROS under irradiation by a 1500 mW/cm² Xe lamp with or without a UV-Vis filter [70]. Fig.

Fig. 8. XPS spectra of the as-prepared UCNPs/SiO₂/CdS/TiO₂ composite nanotubes: (a) survey spectrum and (b–j) Cd 3d, Er 4d, Na 1s, S 2p, Si 2p, Ti 2p O 1s, and F 1s spectral regions, respectively.

10 shows fluorescence spectra of aqueous TPA solution in presence of the as-prepared composites after varying irradiation times. The wide fluorescence peak at 421 nm was at-

tributed to the formation of 2-hydroxy-terephthalic acid (TAOH). This indicated that $\cdot\text{OH}$ was generated in presence of the as-prepared composites under irradiation by UV-Vis-IR and IR light (the latter obtained by using a UV-Vis filter) [70]. More $\cdot\text{OH}$ was generated with increasing irradiation times. The as-prepared samples should therefore exhibit photocatalytic degradation capability under excitation by IR light or simulated solar light using a Xe lamp.

Photocatalytic experiments were carried out in a beaker

Fig. 9. (a) Fluorescence spectra of UCNPs, UCNPs/SiO₂/CdS/PVP, and the UCNPs/SiO₂/CdS/TiO₂ nanocomposites, under excitation by a 980 nm CW laser. (b) UV-Vis absorption spectra of CdS, UCNPs/CdS/PVP/SiO₂, and the UCNPs/SiO₂/CdS/TiO₂ nanocomposites.

Scheme 1. Illustration of the production of reactive oxygen species for the photocatalytic degradation of dyes.

Fig. 10. Fluorescence spectra of TAOH at an excitation wavelength of 315 nm, illustrating the formation of $\cdot\text{OH}$ in presence of the as-prepared composites during irradiation by a 1500 mW/cm^2 Xe lamp (a) without and (b) with an UV-Vis filter.

using 50 mL of RhB solution with an initial concentration of 4.7 $\text{mg}\cdot\text{L}^{-1}$, in presence of 20 mg of different photocatalysts. Fig. 11a–c shows that more than 90% of RhB was decomposed in

25 min, during excitation by simulated solar light from a 250 W Xe lamp without a filter. More than 50% of RhB was decomposed in 70 min, during IR irradiation from a Xe lamp with an UV-Vis filter. For comparison, different photocatalysts including UCNP $\text{s}/\text{SiO}_2/\text{CdS}/\text{PVP}$ and UCNP s were also subjected to photocatalysis experiments. The results are shown in Fig. 11b and c, and demonstrated that the UCNP $\text{s}/\text{SiO}_2/\text{CdS}/\text{TiO}_2$ composite nanotubes had enhanced photocatalytic performance towards the degradation of RhB. Many studies have reported that ROS can decompose RhB to CO_2 [71,72]. TOC analysis was also carried out to confirm the degradation of RhB. TOC values of 5.2 and 0.5 $\text{mg}\cdot\text{L}^{-1}$ were obtained in RhB solutions before and after the photocatalysis experiment, respectively. This showed that most RhB was oxidized to CO_2 . Three consecutive experiments using recycled photocatalyst showed that the TiO_2 composite nanotubes had excellent chemical ability (Fig. 11d).

4. Conclusions

A colloidal process and electrospinning were used to fabricate UCNP $\text{s}/\text{SiO}_2/\text{CdS}/\text{TiO}_2$ composite nanotubes, which averaged several micrometers in length and 20 nm in thickness. The fluorescence emission of the UCNP s was greatly quenched upon excitation using a 980 nm CW laser, which demonstrated their fluorescence energy transfer efficiency. The composite TiO_2 nanotubes showed excellent photocatalytic performance towards the degradation of RhB dye. This photocatalyst makes efficient use of the full solar spectrum, and provides a means to overcome energy shortages and environmental protection.

Fig. 11. (a) UV-Vis absorption spectra of RhB catalyzed by the UCNP $\text{s}/\text{SiO}_2/\text{CdS}/\text{TiO}_2$ composite nanotubes after different irradiation times from a 250 W Xe lamp (UV-Vis-IR) without a filter. Kinetic curves of RhB degradation in the presence of different photocatalysts under irradiation by a Xe lamp (b) without and (c) with a UV-Vis filter, which cut out UV and visible wavelengths, respectively. C_0 and C_t are the concentration of the initial solution and at irradiation time t (min), respectively. (d) Kinetic curves of RhB degradation in the presence of UCNP $\text{s}/\text{SiO}_2/\text{CdS}/\text{TiO}_2$ composite nanotubes during three consecutive photocatalytic experiments.

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Graphical Abstract

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TiO₂ composite nanotubese embedded with CdS and upconversion nanoparticles for near infrared light driven photocatalysisWanni Wang, Fu Zhang, Chuanling Zhang, Yang Wang, Wei Tao *, Sheng Cheng *, Haisheng Qian *
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TiO₂ nanotubes embedded with a high proportion of NaYF₄:Yb/Tm@NaYF₄:Yb/Er upconversion nanoparticles and CdS nanoparticles are prepared using a colloidal solution method and electrospinning, and show excellent fluorescence energy transfer efficiency and photocatalytic performance.

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内嵌硫化镉与上转换纳米颗粒的二氧化钛复合纳米管用于近红外光驱动光催化

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摘要: 由于近红外光在太阳光谱中占44%, 因此, 近红外光驱动的光催化剂的研制具有十分重要的意义. 上转换发光材料可将低能量的近红外光子转换为高能光子, 这种高能光子可以通过构建荧光共振转移系统将能量转移并活化量子效率较高的半导体材料, 对于太阳能的转化利用具有潜在的应用前景. 在本文中, 通过胶体化学的过程在电纺丝制备的内嵌CdS纳米颗粒以及上转换荧光纳米颗粒(UCNPs)的二氧化硅复合纳米纤维表面外延生长一层二氧化钛层, 通过高温煅烧得到二氧化钛复合纳米管. 我们通过二氧化硅结构将CdS纳米颗粒与上转换荧光纳米颗粒紧紧束缚在一起, 实现较高的荧光共振能量转移. 而且, 选择 β -NaYF₄:Yb(30%), Tm(0.5%)@NaYF₄:Yb(20%), Er(2%)作为纳米能量转换器, 替代以前研究工作中使用的 β -NaYF₄:Yb(30%), Tm(0.5%)或者 β -NaYF₄:Yb(30%), Tm(0.5%)@NaYF₄纳米颗粒, 来进一步提高近红外光的转换效率. 通过透射电子显微镜照片很清楚的观察到制备的TiO₂复合纳米管内部内嵌有大量的CdS与上转换纳米颗粒. 通过X-射线衍射以及X-射线光电子能谱能仪器对产物的物相以及表面的化学组成进行了细致的表征. 结果显示, 通过本实验方法已经成功获得了TiO₂复合纳米管.

用稳态与瞬态荧光仪研究了最终样品的荧光性质. 研究结果揭示, 与上转换纳米颗粒以及二氧化硅复合纳米纤维相比, 复合二氧化钛纳米管可以将上转换荧光纳米颗粒的(UV-Vis)部分荧光完全淬灭了. 特别是, 铒离子的荧光(650 nm)也被有效淬灭转移, 说明本研究采用 β -NaYF₄:Yb(30%), Tm(0.5%)@NaYF₄:Yb(20%), Er(2%)纳米能量转换器, 可以提高近红外光的转换效率, 紫外-可见吸收光谱证实, 这种二氧化钛纳米管在紫外-可见光区中的吸收光谱与 β -NaYF₄:Yb(30%), Tm(0.5%)@NaYF₄:Yb(20%), Er(2%)纳米颗粒的荧光光谱具有较大的重叠, 使得上转换荧光纳米颗粒与CdS以及二氧化钛

组分之间的荧光共振转移的效率大大提高,进而会显著提高光催化的效果.以罗丹明染料作为污染物为模型,我们研究了罗丹明染料在氙灯下或者近红外光光照下的光催化分解实验.研究表明,90%的罗丹明染料分子在20 min内就被降解掉,效率高于其它近红外光催化剂.上转换荧光纳米颗粒的能量转换效率可以得到大幅度提高,本研究工作中制备的光催化剂利用太阳能的效率将会得到极大提高,在未来为能源危机以及环境保护提供一种可供选择的方法与技术.

关键词: 二氧化钛纳米管; 上转换纳米颗粒; 能量转移; 光催化; 纳米转换器

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