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UV-visible and near-infrared active NaGdF₄: Yb: Er/Ag/TiO₂ nanocomposite for enhanced photocatalytic application Natarajan Prakash,[†] Dheivasigamani Thangaraju,[‡] Rajan Karthikeyan,[†] Mukannan Arivanandhan,[§] Yosuke Shimura[‡] and Yasuhiro Hayakawa^{†,‡,*}

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Abstract

near infra-red (NIR) active NaGdF₄:Yb:Er/Ag/TiO₂ nanocomposite A photocatalyst was successfully synthesized by one-pot thermal decomposition method. composite structure, morphology and elemental mapping of synthesized NaGdF₄:Yb:Er/Ag/TiO₂ nanocomposite was characterized by X-ray diffraction and transmission electron microscopy analysis. The energy transfer among NaGdF₄:Yb:Er, Ag, and TiO_2 were revealed by upconversion photoluminescence measurement under 980 nm. The Ag and NaGdF₄ nanoparticles enhanced the visible and NIR light absorption property of NaGdF₄:Yb:Er/Ag/TiO₂ nanocomposite. NIR and UV-visible light induced photocatalytic study of NaGdF₄:Yb:Er/Ag/TiO₂ composite was examined by Rhodamine B degradation. The energy transfer among NaGdF₄:Yb:Er, Ag, and TiO₂ influenced the photocatalytic activity significantly in NIR irradiation. The catalysts produced oxidative species during NIR irradiation, which are responsible for photocatalytic degradation of Rhodamine B. NaGdF₄:Yb:Er/Ag/TiO₂ showed photocatalytic activity under NIR and UV-visible radiation (full solar irradiation), which is superior compared to UV or visible light active photocatalyst. The study provided a UV-visible and NIR-responsive photocatalyst with its energy transfer mechanism.

Keywords: Photocatalysis, upconversion, NaGdF₄, TiO₂, Ag, nanocomposite

Introduction

Increasing population around the world leads to increased environmental pollution and energy deficient. Photocatalysis is one of the promising technologies, which solve the environmental problems since it utilizes vast abundant and cheap solar energy.^{1–3} TiO₂ is one of the most gifted photocatalysts because of its outstanding physical and chemical properties such as high oxidative power, chemical and photostability, biocompatible nature and commercially cheap.^{4–7} The UV light active TiO₂ (3.2 eV) only utilizes 5 % of sunlight. Therefore, there is still a huge energy (visible light 49 %, near infra-red (NIR) 46 %) available in the sunlight, which isn't harvested by TiO₂ itself.^{8,9} Numerous strategies have been tried to extend the utilization of sunlight, such as doping,^{10–12} noble metal deposition,¹³ dye sensitizing,¹⁴ and mixed semiconductor composites.^{15–17} However, complete absorption of solar spectrum has not been achieved yet. The modifications for shifting the absorption edge of TiO₂ up to the visible light (up to 725 nm) have been done, however the NIR light is still not used.^{18,19} Researchers are facing numerous challenges to develop an ideal catalyst, which is active in the entire solar light region without losing their photocatalytic efficiency.

The semiconductor catalysts having upconversion luminescence are paving a path to utilize NIR light for the photo-catalytic application.^{20,21} Upconversion phosphor emits the high energy light (visible and UV light) by NIR light (980 nm) excitation via a nonlinear process.²² The direct doping of upconversion ions (Tm, Er, Yb/Tm, Yb/Er) on semiconductor catalyst did not show efficient conversion.^{23–25} Qin et.al initially reported TiO₂ coated YF₃:Yb:Tm host for photodegradation of methylene blue under NIR

irradiation.²⁶ There are limited papers reporting the upconversion based NIR photocatalysis.^{27–29} Tang et.al investigated NaYF₄:Yb³⁺,Tm³⁺@TiO₂ core-shell structures for methylene blue degradation and discussed the energy transfer mechanism under NIR irradiation.³⁰ The structure utilizes only the UV and NIR light, the visible light is unused. The visible light photocatalytic activity of NaYF₄:Yb³⁺,Tm³⁺/TiO₂ was improved by linking CdS nanostructures.³¹ Selection of host lattice, upconversion doping ions and photocatalyst are important to design full solar light spectrum active photocatalyst. Fluoride-based phosphors such as NaGdF₄,³² NaYF₄,³³ YF₃,²⁶ and CaF₂³⁴ were reported as efficient hosts for upconversion ion doping because of their low phonon energy, high luminous intensity, and excellent chemical stability. NaGdF₄-based upconversion phosphors have significantly drawn attention due to their bright upconversion luminescence emission along with magnetic property, which allows for separation of the particles magnetically.^{35,36}

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The doped Yb absorbs the NIR excitation and transfers the energy nonradioactively to co-dopants such as Er^{3+} , Tm^{3+} and Ho^{3+} .^{36,37} The dopants were excited during the two-photon or multi-photon process and de-excited to the ground state with high energy light emission. The photocatalytic reaction could be initiated by absorbing the emitted light from upconversion particles through appropriate semiconductor composite.³¹ Yb³⁺-Tm³⁺ upconversion ions are mainly used as a dopant in the NIR driven rare earth fluorides/TiO₂ composite photocatalyst since they emit UV light under NIR excitation.³⁰ The energy transfer process activates the photocatalytic reaction on the catalyst surface (TiO₂). However, visible light conversion from NIR light involves fewer anti-stoke shifts, which is more profitable than UV light conversion from NIR

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light.²⁹ Yb³⁺-Er³⁺ ions would be a promising dopant for visible light emission, which emits visible light (650, 540, 520 nm) upon NIR excitation.^{38,39}

On the other hand, nano Ag shows size dependable surface plasmon resonance (SPR) absorption property in the visible region which contributes a new prospect to overcome the limitation of visible light absorption of the photocatalysts.⁴⁰ A collective oscillation of free electrons in the plasmonic Ag structure produces a strong light absorption and it can generate a strong electric fields near the surface.⁴¹ These properties can be useful for photocatalytic reaction. Surface plasmon sensitized Ag photocatalysts showed promising photocatalytic activity in the visible light region.⁴²⁻⁴⁶ The absorption range of Ag lies on the emission position of upconversion phosphor, and it enhances local field which results in an enhancement of the energy transfer from Yb³⁺ to Er^{3+,47,48} Therefore, Ag can be used to absorb the emitted visible light from the upconversion phosphor and transfer electrons to semiconductor catalyst. Xu et.al studied plasmonic Au based NaYF4:Yb3+,Tm3+, Er3+/TiO2 NIR photocatalyst for solar utilization.⁴⁹ Ma et.al utilized Ag complete NIR responsive in NaYF₄:Yb,Tm@TiO₂ catalyst to enhance electron-hole pair separation.⁵⁰ However, plasmonic silver utilization with upconversion phosphor has not been demonstrated yet. The fabrication of lanthanide doped upconverting phosphor, Ag and TiO₂ in a single system may allow the effective consumption of UV, visible and NIR light for photocatalytic purpose via plasmonic and upconversion property.

In this work, NIR active NaGdF₄:Yb:Er/Ag/TiO₂ nanocomposite catalyst was synthesized by a one-pot thermal decomposition method. Structural, morphological and energy transfer process of NaGdF₄:Yb:Er/Ag/TiO₂ were investigated and compared with the NaGdF₄:Yb:Er/Ag, NaGdF₄:Yb:Er/TiO₂ composites, which were synthesized

by the similar procedure. Photocatalytic activities of synthesized nanocomposite catalysts were evaluated by Rhodamine B dye degradation experiments under NIR light (980 nm) and UV-visible light (300 – 600 nm). The possible photocatalytic reaction pathways were discussed. In this method, Nano-scaled (less than 25 nm) upconversion host (NaGdF₄) and Ag particles are synthesized which increase the surface contact among the NaGdF₄, Ag, and TiO₂ particles. The up converting host and Ag nanoparticles were closely contact with each other as well as TiO₂ which is the major advantages in this structure. These structure allows the efficient charge and/or energy transfer among NaGdF₄:Yb:Er, Ag and TiO₂ particles and enhance the plasmonic and upconversion phenomenon in the photocatalytic reaction. The synthesized catalyst would effectively use all the spectrum regions of the solar light.

2. Experimental section:

2.1 Materials

Titanium (IV) isopropoxide (Ti(OCH(CH₃)₂)₄, 95 %, Wako), silver nitrate (AgNO₃, Wako), oleylamine ($C_{18}H_{35}NH_2$, 70 %, Wako), gadolinium oxide (Gd_2O_3 , 99.9 %, Wako), ytterbium oxide (Yb₂O₃, 99.9 %, Wako), erbium oxide (Er₂O₃, 99.9 %, Wako), sodium trifluoroacetate (CF₃COONa, 98 %, Wako), trifluoro acetic acid ($C_2HF_3O_2$, 99 %, Wako) were used as precursors. All the oxides were dissolved in trifluoro acetic acid to form trifluoroacetate, which was dried at 80 °C and preserved in an airtight glass bottle. Chemicals such as ammonia (28 %, Wako), acetone (99.5 %, Wako), cyclohexane (99.5 %, Wako) and ethanol (99.5 %, Wako) were used as purchased. Photocatalytic activity of the catalyst was studied using Rhodamine B ($C_{28}H_{31}ClN_2O_3$, Wako) as a model pollutant.

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2.2 Synthesis of NaGdF₄:Yb:Er/Ag/TiO₂ composite nanomaterials

NaGdF₄:Yb:Er/Ag/TiO₂ nanocomposite was synthesized by the high-temperature thermal decomposition method. The schematic diagram of the synthesis procedure is shown in Fig. 1. The precursors for $NaGdF_4$ such as CF_3COONa (6 mmol), Gd(CF₃COO)₃ (2.34 mmol), Yb(CF₃COO)₃ (0.6 mmol) and Er(CF₃COO)₃ (0.06 mmol) were dissolved in a 15 mL of oleylamine solvent in a round bottom (RB) flask (100 mL) attached with a cooling condenser. The RB flask was evacuated with a vacuum pump and the reaction temperature raised to 160 °C. The reaction was kept at 160 °C for 30 min to remove moisture and O_2 in oleylamine. The reaction solution was raised to 330 °C to initiate the decomposition of precursors. The reaction was carried out for 1 h at 330 °C under N₂ flow. The resultant product was cooled to 50 °C and silver nitrate (2) mmol) was added to the NaGdF₄:Yb:Er–olevlamine solution. The reaction temperature was increased to 150 °C and kept for 1 h under N_2 atmosphere to obtain NaGdF₄:Yb:Er/Ag composite. The reaction solution colour was turned to red, specifying the formation of Ag particles. To the resultant solution, 3 mL of Titanium isopropoxide was added and the temperature of the solution again raised to 280 °C and kept for 1 h under air atmosphere. The resulting NaGdF₄:Yb:Er/Ag/TiO₂ composite solution was cooled to room temperature. The sample was precipitated, centrifuged and thoroughly washed several times with hexane, acetone and ethanol solvents. $NaGdF_4$: Yb:Er/Ag and NaGdF_4: Yb:Er /TiO₂ composites were synthesized by the same procedure as mentioned for the comparison of luminescence and catalytic activity studies. The synthesized NaGdF₄:Yb:Er/Ag/TiO₂ catalyst was taken in a 20 mL of ammonia and ethanol mixed solution (50 mL/50 mL) and stirred for 30 min to remove the surface oleylamine. The reaction mixture was centrifuged at 6000 rpm and the

sample redispersed again in a 20 mL of ammonia/ethanol solution. The procedure was repeated four times, the obtained product was washed well with water until pH 7. The sample was dried and used for photocatalytic studies.

2.3 Photocatalytic degradation of Rhodamine B

Photocatalytic performance of NaGdF₄:Yb:Er/Ag/TiO₂ nanocomposite was evaluated by monitoring degradation of Rhodamine B dye molecules under NIR irradiation. The photocatalytic experiment was as follows: 8 mg of synthesized catalyst was suspended in a 5 mL of Rhodamine B (5 mg/L) solution and stirred for 1 h in the dark to reach adsorption–desorption equilibrium of the dye with the catalyst before irradiation. The Rhodamine B solution was irradiated with a 980 nm NIR source (1.5 W). 1.5 mL of solution was taken out from the reaction mixture at constant time intervals (3 h). The absorbance of Rhodamine B was monitored at 554 nm using a UV-Vis spectrophotometer and then the solution was put back into the cell. To evaluate UV-visible light driven photocatalytic activity, 40 mg of catalyst was added into a lab-made borosilicate reactor containing 40 mL of Rhodamine B solution (5 mg/L). The solution was illuminated with a UV-visible light source (500 W, 300-600 nm). 3 mL of suspensions were withdrawn from the reaction mixture at regular irradiation time intervals. The suspension was centrifuged to remove catalysts and absorbance was measured.

2.4 Characterization

The crystal structures of the synthesized composite catalysts were identified by powder X-ray diffraction (XRD) using a Rigaku X-ray diffractometer RINT-2200 (Cu K α radiation, λ =1.54178 Å)). JEOL JEM 2100F HRTEM (200 kV acceleration voltage)

was used for transmission electron microscope (TEM), energy dispersive X-ray spectroscopy (EDX) and mapping images. The oxidation states of the catalyst were analyzed with X-ray photoelectron spectroscopy (XPS) (ESCA 3100, Shimadzu). Diffuse reflectance spectra (DRS) and ultraviolet-visible absorption spectra were analyzed by UV-VIS-NIR spectrophotometer (JascoV-670). Photoluminescence (PL) spectra were recorded in the range of 350–850 nm using a fluorescence spectrophotometer (Jasco FP - 8600). Photocatalytic measurement was performed using UV-visible light source (MAX 303, Asahi, Japan) and 980 nm continuous NIR laser of Changchun New Industries Optoelectronics Technology Co., Ltd.

4. Result and discussion

4.1. Structural, morphological and elemental studies

The crystal phases of synthesized NaGdF₄:Yb:Er, NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag/TiO₂ samples were identified by XRD analysis. The acquired patterns of NaGdF₄:Yb:Er, NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag/TiO₂ were compared in Fig. 2. Recorded reflections of NaGdF₄:Yb:Er (Fig. 2a) were well matched with a hexagonal crystal structure of NaGdF₄ (JCPDS Card No. 27-0699). A low intense peak appeared at 28.2° (•) corresponded to the cubic crystalline nature of the NaGdF₄ (JCPDS Card No. 27-0697), which indicated a small amount of cubic phase present in the sample. When Ag is added, the characteristic Ag peaks appeared at 38.2°, 44.3°, and 64.4°, which corresponded (111), (200), and (220) planes of face centred-cubic structure of silver particle (JCPDS Card No. 01-087-0720), which indicated the presence of metallic silver in NaGdF₄:Yb:Er/Ag composite (Fig. 2b). XRD pattern of

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NaGdF₄:Yb:Er/TiO₂ shows anatase phase TiO₂ peaks (JCPDS Card No. 21-1272), which are marked by the lattice planes in (Fig. 2c) along with NaGdF₄ reflections. The XRD peaks of NaGdF₄, Ag and TiO₂ were observed for NaGdF₄:Yb:Er/Ag/TiO₂ as shown in Fig. 2d, which confirmed the formation of composites.

The morphology and size of the nanocomposite were studied by TEM images and elemental mapping analysis. Fig.3.1 shows the NaGdF₄:Yb:Er particles which were about 10 nm in diameter. NaGdF₄:Yb:Er/Ag (Fig. 3.2) composites exhibited distinct Ag and NaGdF₄ particles. TEM images of NaGdF₄:Yb:Er/Ag/TiO₂ composite consisted of a foam-like structure with sphere-like particles dispersed everywhere (Fig.3.3). The elemental mapping of individual elements Na, Gd, F, Yb, Ag, Ti, and O (Fig (3.5 b) -(3.5 h) evidently showed the existence of NaGdF₄:Yb:Er and Ag particles in the TiO₂ foam-like structure. The elements were confirmed with EDS spectrum as shown in Fig. 3.5 i. The elemental mapping of Gd (Fig. 3.5 c) and Ag (Fig. 3.5 f) displayed the spherical shaped NaGdF₄:Yb:Er and Ag particles with diameter ranged between 8-20 They were dispersed on the fine TiO_2 grains. Over all size of nm. NaGdF₄:Yb:Er/Ag/TiO₂ nanocomposite particles were in the range of 100 – 200 nm. The spacing of lattice fringes 0.52, 0.23 and 0.35 nm (Fig. 3.4) indicated the (100), (111) and (101) planes of hexagonal NaGdF₄ cubic Ag, and anatase TiO₂, respectively. TEM and mapping suggested that $NaGdF_4$ and Ag nano particles formed a composite structure with TiO₂ particles.

The chemical environment of the elements present in the NaGdF₄:Yb:Er/Ag/TiO₂ composite were analyzed using XPS analysis. The XPS spectrum of Ti 2p, O 1s, and Ag 3d orbitals are measured as shown in Fig. 4 (a-c). The

two peaks Ti $2p_{3/2}$ and Ti $2p_{1/2}$ are positioned at 458.8 eV and 464.5 eV, which attributed to the Ti⁴⁺ state of anatase TiO₂. Surface disorders led to Ti³⁺ formation, which appeared at 457.3 eV. The asymmetric O 1s peak was deconvoluted into two peaks centered at 530.3 and 532.1 eV, which are related to the lattice oxygen of TiO₂ and hydroxyl oxygen present on the surface, respectively. The two peaks, Ag 3d $_{5/2}$ and Ag 3d $_{3/2}$ separated with ~6 eV were located at 367.9 and 373.9 eV, which designated the metal state of Ag particle. A small quantity of silver exists as an oxide form, observed around ~367eV. F 1s peak of NaGdF₄, NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag/TiO₂ was studied and compared in Fig 4. (d). The F 1s peak of NaGdF₄:Yb:Er/Ag (686.6 eV) and NaGdF₄:Yb:Er/Ag/TiO₂ (685.1 eV) were shifted from the F 1s peak of NaGdF₄:Yb:Er at 686.0 eV. This suggested the chemisorption of NaGdF₄ particle with Ag and TiO₂. The Yb 4d and Er 4d peaks (Fig. 4 (e)) were observed at 172.6 eV and 188.4 eV respectively, well matched with reported values, confirming the doping on NaGdF₄.⁵¹

4.2 Optical studies

Optical properties of synthesized composite catalysts were analyzed by UVvisible absorption measurement and upconversion luminescence analysis. Recorded absorption spectra of NaGdF₄:Yb:Er, NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag/TiO₂ are shown in Fig. 5 (a). Absorption spectrum of NaGdF₄:Yb:Er (black curve) showed small absorption peaks of Er^{3+} (488, 520, 540 and 653 nm). For NaGdF₄:Yb:Er/Ag (red curve), a wide absorption peak (350-750 nm) was observed in the visible region, which corresponded to the localized surface plasmon resonance peak delivered by Ag NPs.

The absorption spectrum of NaGdF₄:Yb:Er/Ag/TiO₂ (blue curve) showed the wide absorption peaks of Ag combined with TiO₂ absorption in the UV region.

Upconversion luminescence spectra of as-synthesised NaGdF₄:Yb:Er, NaGdF₄:Yb:Er/Ag, NaGdF₄:Yb:Er/TiO₂ and NaGdF₄:Yb:Er/Ag/TiO₂ nanoparticles were studied under an excitation wavelength of 980 nm as shown in Fig 5 (b). The luminescence spectra showed four significant peaks at 523, 542, 656 and ~ 800 nm. which corresponded to the transitions of ${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$, ${}^{4}F_{9/2}$ and ${}^{4}I_{9/2}$ levels to the ${}^{4}I_{15/2}$ level of Er³⁺, respectively.⁵¹⁻⁵³ After addition of TiO₂ to NaGdF₄, the upconversion emission intensities were decreased slightly because the excitation light was shielded by TiO₂ particles on the surface of the NaGdF₄:Yb:Er. The peak intensities of NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag/TiO₂ were drastically decreased because of silver and TiO₂ addition to the NaGdF₄:Yb:Er particles. Fig. 5 (c) shows the visual emitting images of NaGdF₄:Yb:Er, NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag/TiO₂ excited by NIR 980 nm laser. The brightness of green color light of NaGdF₄:Yb:Er was reduced and turned to weak red (${}^{4}I_{9/2}$ - ${}^{4}I_{15/2}$) by the addition of Ag and TiO₂. respectively. Ag particles induced larger reduction of green light emission than red light since the absorption maximum exactly matched with the green light region. These observations can be explained by the schematic diagram as shown in Fig. 6, which shows the photoluminescence and NIR light influenced photocatalytic reaction mechanism of the NaGdF₄:Yb:Er/Ag/TiO₂ composite. It is well known that upconversion phosphors can convert longer wavelength NIR radiation into shorter wavelength light (UV or visible light) through a two or multiphoton absorption mechanism ^{39,51}. During the excitation of NaGdF₄:Yb:Er under 980 nm by NIR laser, Yb³⁺ ion acts as a NIR sensitizer, which absorbs the photons (980 nm), and results in an

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electron excitation from ${}^{2}F_{7/2}$ to ${}^{2}F_{5/2}$ level. The excited Yb³⁺ transports energy to Er³⁺ ions during relaxation. The process induced excitation from ${}^{4}I_{15/2}$ to ${}^{4}I_{11/2}$ in Er³⁺ ions. Two or more similarly excited photons were populated at higher energy levels of Er³⁺ (${}^{4}F_{9/2}$, ${}^{4}S_{3/2}$ and ${}^{2}H_{11/2}$).²⁹ The excited electrons of Er³⁺ relaxed to the ground state with the emission of visible light. The absorption range of the Ag overlaps the emitted visible light of NaGdF₄:Yb:Er, which indicated that the emitted light from NaGdF₄:Yb:Er could be recaptured by Ag. This reabsorption led to the strong decrement of luminescent intensity. TiO₂ encapsulation over the NaGdF₄:Yb:Er/Ag led to a further decrease of intensity, indicating the energy transfer from Ag to TiO₂ particles. Similar kind of luminescent intensity reduction was observed and reported for NaGdF₄:Yb:Er/Au and NaYF₄:Yb:Er/C-doped TiO₂ composites.^{29,48}

4.3 Photocatalytic studies

Rhodamine B was utilized as a model pollutant to demonstrate the performance of the prepared catalysts under NIR irradiation (980 nm). Dye degradation (C/C_0) was calculated from the initial (C_0) and absorbance values (C) of Rhodamine B at different interval of time. The absorbance of Rhodamine B decreased gradually because of the photocatalytic degradation reaction catalyzed by NaGdF₄:Yb:Er/Ag/TiO₂ nanocomposites as shown in Fig. 7. The time-dependent relative concentration ratios (C/C₀) of Rhodamine B was studied for NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag/TiO₂ as shown in Fig. 8 (a). There is no degradation of Rhodamine B in the absence of a catalyst at NIR irradiation. The C/C₀ value against time revealed that NaGdF₄:Yb:Er/Ag/TiO₂ degraded 40 % of Rhodamine B under 18 h NIR irradiation. However, NaGdF₄:Yb:Er/Ag were able to degrade only 21 % Generally, TiO₂ and Ag

were inactive in NIR light. In the case of NaGdF₄:Yb:Er/Ag, the emitted upconversion light of NaGdF₄:Yb:Er was recaptured by Ag particles and generated hot electrons and holes. In NaGdF₄:Yb:Er/Ag/TiO₂, during surface plasmon excitation the electrons of Ag obtained sufficient energy to overcome schottky barrier and transferred to TiO₂ surface by charge transfer mechanism.⁵⁴ Hence, the recombination of photogenerated electron and hole pair minimized significantly and improved the electron – hole pair separation in Ag nano particles. Photo-generated holes in Ag particles plays a vital role to oxidize the Rhodamine B into oxidized products (CO₂ and H₂O). The moved electrons to the conduction band of TiO₂ generated $^{\circ}O_2$ radicals which in turn converted to $^{\circ}OH$ radicals. The photo generated $^{\circ}OH$ radicals (and $^{\circ}O_2$) actively oxidized the conjugated chromophore of the dye molecule. The $^{\circ}OH$ formation reaction are shown in equation (1.1) - (1.5).

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$$O_2 (TiO_2) + e^- \longrightarrow O_2^- (TiO_2)$$
(1.1)

$$\bullet O_2^-(TiO_2) + H^+ \longrightarrow HO_2^{\bullet}(TiO_2)$$
(1.2)

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$$
(1.3)

$$H_2O_2 + O_2 \bullet \bullet OH + OH + O_2$$
(1.4)

 $h^+(Ag) + RB$ \longrightarrow degraded or mineralized product (1.5)

•OH (or O_2^{\bullet}) + RB \longrightarrow degraded or mineralized product (1.6)

From the Fig. 8a, NaGdF₄:Yb:Er/Ag/TiO₂ showed higher photocatalytic activity than the NaGdF₄:Yb:Er/Ag. It confirmed that Ag acts as an intermediate carrier for the keen energy transfer between NaGdF₄:Yb:Er and TiO₂. For more confirmation, Terephthalic acid fluorescence probe test was carried to identify the formation of

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oxidative 'OH radicals on the surface of the nanocomposite during NIR irradiation.^{27,30} Fig. 8b shows the fluorescence spectra of hydroxy terephthalic acid monitored at 424 nm under 320 nm excitation. Terephthalic acid didn't show any fluorescent emission, but the non-fluorescent terephthalic acid produced fluorescent emission at 424 nm when it became hydroxyl terephthalic acid. NaGdF₄:Yb:Er/Ag/TiO₂ catalyzed terephthalic acid photocatalytic reaction driven by NIR irradiation produced hydroxy terephthalic acid intermediate when exposed by 980 nm light. The gradual increment in the intensity with time confirmed the increasing concentration of hydroxy terephthalic acid. The intensity change means 'OH radical generated during the reaction.

For further photocatalytic investigation, the photocatalytic degradation was performed under UV-visible light irradiation and the results are shown in Fig.9 (a-d). The absorption spectra of Rhodamine B decreased gradually with NaGdF₄:Yb:Er/TiO₂ (a) NaGdF₄:Yb:Er/Ag (b), and NaGdF₄:Yb: $Er/Ag/TiO_2$ (c) catalysts under UV-visible light irradiation. Two different degradation patterns were observed for the composite catalysts. NaGdF₄:Yb:Er/TiO₂ catalysed photodegradation curves of Rhodamine B hypsochromic shifted to shorter wavelength (~498 nm) during 30 min irradiation; after that the absorption position did not change, but the absorption intensity decreased to nearly zero. NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag/TiO₂ catalysed reaction showed the traditional degradation pattern.⁵⁵ The hypsochromic shift can be explained through two different cleavage pathway of Rhodamine B molecule under UV-visible irradiation. Generally, Rhodamine B adsorbs on the surface of TiO₂ via carboxylic group (COOH).⁵⁶ The oxidative species of TiO_2 are actively attacked the conjugated chromophore ring, which is identified from the decrease of Rhodamine B absorption at 554 nm. On the other hand, few reports suggest that surface fluorination or anionic

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surfactant modification on TiO₂ convert the adsorption modes of TiO₂.⁵⁶ Surface fluorination on TiO_2 increases more polarity (negative charge) on the surface. Therefore, Rhodamine B tend to adsorb through -NEt₂ (cationic group). This type of adsorption led to the cleavage of amine group initially and produce intermediate rhodamine (498 nm).^{57,58} This interpretation is supported by the adsorption of Rhodamine B on the catalyst surface. The adsorption (%) of NaGdF₄:Yb:Er/TiO₂ NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag/TiO₂ are 48, 36, 15 % respectively, calculated from the absorbance difference between the fresh dye and before irradiation (0 min). The Rhodamine B adsorbed on the NaGdF₄:Yb:Er/TiO₂ surface was much higher than that of $NaGdF_4$: Yb: Er/Ag and NaGdF_4: Yb: Er/Ag/TiO₂ composites. The adsorption behaviour attributed to the increased surface area and polarity of the composites. In NaGdF₄:Yb:Er/TiO₂ composite NaGdF₄ has changed the surface characteristic of NaGdF₄:Yb:Er/TiO₂, and orient the Rhodamine B adsorption through amine group. The adsorption on TiO₂ facilitated the N-de-alkylation of Rhodamine B (Fig. 9 e) and produce Rhodamine, which was observed at 498 nm (Fig.9 a). The resultant intermediate degraded gradually with the irradiation of light. It is understood that for semiconductor based photocatalysts adsorption of reactants are very important for enhanced photocatalytic activity. Since it introduces reactants rich environment and reinforce the interaction between reactant and catalyst surface.⁵⁹ On the other hand, for silver nanoparticle containing composites NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag/TiO₂ (Fig. 9 b and c) the absorption intensity of Rhodamine B decreases with slight shift but did not approach to 498 nm. The observation suggested that silver addition to the NaGdF₄ reduces the surface charge of the catalyst by making chemisorption. Therefore, the rhodamine B was predominantly decomposed by typical

conjugated chromophore cleavage pathway rather than N-de-alkylation. Even though, nanocomposite catalysts decomposed the rhodamine B by two different pathways, NaGdF₄:Yb:Er/Ag/TiO₂ composite took only 30 min for almost complete degradation. Fig.9 d shows that NaGdF₄:Yb:Er/Ag/TiO₂ had a higher photocatalytic activity than NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/TiO₂ because of enhanced light absorption and efficient generation of photogenerated species. The results conclude that NaGdF₄ introduced not only up-conversion luminescence emission but also increase of the adsorption of dyes (cationic groups) on the surface of the catalysts. The results exhibited the excellent UV-visible light driven photocatalytic ability of the catalyst.

The reusability of the catalyst was verified under UV-visible irradiation, as shown in Fig. 10. The catalyst showed 97, 95, 92, 94, 80 and 77 % of Rhodamine B degradation for 30 min. The catalyst exhibited nearly equal value for first four cycles. After that, it started to decrease. This might be due to the aggregation of particles during prolonged usage.

5. Conclusions

One-pot thermal decomposition method was developed to synthesize NaGdF₄:Yb:Er/Ag/TiO₂ nanocomposite XRD, TEM, EDS and elemental mapping results confirmed the composite structure of the NaGdF₄:Yb:Er, Ag particles, and TiO₂ nanostructrures. The materials showed excellent luminescent quenching behavior upon 980 nm irradiation by adding Ag and TiO₂ with NaGdF₄:Yb:Er. The emission region of NaGdF₄:Yb:Er overlapped with the absorption range of Ag/TiO₂, which was identified by UV-Vis absorption spectra. The emitted upconversion light was recaptured by Ag/TiO₂ which created a photocatalytic reaction under NIR irradiation. Interestingly,

two different fragmentation pathways were identified for Rhodamine B with the composites under UV-visible light because of the two different adsorption modes. The promising photocatalytic results of NaGdF₄:Yb:Er/Ag/TiO₂ under the UV-visible and NIR lights revealed a new pathway to harvest UV-visible and infra-red light from solar light

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Figure captions:

Fig. 1 schematic diagram of synthesis of β-NaGdF₄:Yb:Er /Ag/TiO₂ nanocomposites

Fig. 2. XRD patterns of (a) NaGdF₄:Yb:Er, (b) NaGdF₄:Yb:Er/Ag, (c)

NaGdF₄:Yb:Er/TiO₂ and (d) NaGdF₄:Yb:Er/Ag/TiO₂

Fig 3. TEM images of (1) NaGdF₄:Yb:Er, (2) NaGdF₄:Yb:Er/Ag, (3) and (4)

NaGdF₄:Yb:Er/Ag/TiO₂; (5a) STEM image, EDS mappings of (b) Na, (c) Gd, (d) F, (e)

Yb (f) Ag, (g) Ti, and (h) O and (i) EDS spectrum of NaGdF₄:Yb:Er/Ag/TiO₂

composite

Fig. 4. XPS binding energy curves of NaGdF₄:Yb:Er/Ag/TiO₂, (a) Ti 2p, (b) O 1s, (c) Ag 3d, (d) F 1s, and (e) Yb 4d and Er 4d

Fig. 5. (a) UV-Vis-NIR absorption spectra, (b) upconversion luminescence spectra, (c) visual fluorescence emission images under 980 nm excitations of NaGdF₄:Yb:Er, NaGdF₄:Yb:Er/Ag and NaGdF₄:Yb:Er/Ag/TiO₂

Fig. 6 Schematic diagram of energy transfer and photocatalytic mechanism among Yb, Er, Ag, TiO₂ in NaGdF₄:Yb:Er/Ag/TiO₂ nanocomposite catalyst

Fig. 7. NaGdF₄:Yb:Er/Ag/TiO₂ catalyzed degradation of Rhodamine B at constant irradiation time (3 h) under NIR irradiation (980 nm)

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Fig. 8. (a) Relative ratio (C/C_0) of Rhodamine B at different time catalyzed by NaGdF₄:Yb:Er/Ag/TiO₂ and NaGdF₄:Yb:Er/Ag composites under NIR (980 nm) (b) Terephthalic acid fluorescence spectra at different time catalyzed by NaGdF₄:Yb:Er/Ag/TiO₂ under NIR irradiation

Fig.9. Rhodamine B degradation spectra with different catalysts (a) NaGdF₄:Yb:Er/TiO₂ (b) NaGdF₄:Yb:Er/Ag, (c) NaGdF₄:Yb:Er/Ag/TiO₂; (d) relative absorbance of Rhodamine B with three different catalyst under UV-visible light irradiation; (e) Rhodamine B structural change with NaGdF₄:Yb:Er/TiO₂ under UV-visible light irradiation.

Fig. 10. Rhodamine B degradation with NaGdF₄:Yb:Er/Ag/TiO₂ under UV-visible light irradiation from the first to sixth cycles.

Thermal decomposition method $CF_3COON_a + Gd(CF_3COO)_3 + Yb(CF_3COO)_3$



Fig. 1 schematic diagram of synthesis of β-NaGdF₄:Yb:Er /Ag/TiO₂ nanocomposites



Fig. 2. XRD patterns of (a) NaGdF₄:Yb:Er, (b) NaGdF₄:Yb:Er/Ag, (c) NaGdF₄:Yb:Er/TiO₂ and (d) NaGdF₄:Yb:Er/Ag/TiO₂







Fig 3. TEM images of (1) NaGdF₄:Yb:Er, (2) NaGdF₄:Yb:Er/Ag, (3) and (4) NaGdF₄:Yb:Er/Ag/TiO₂; (5a) STEM image, EDS mappings of (b) Na, (c) Gd, (d) F, (e) Yb (f) Ag, (g) Ti, and (h) O and (i) EDS spectrum of NaGdF₄:Yb:Er/Ag/TiO₂ composite



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Fig. 7. NaGdF₄:Yb:Er/Ag/TiO₂ catalyzed degradation of Rhodamine B at constant irradiation time (3 h) under NIR irradiation (980 nm)



Fig. 8. (a) Relative ratio (C/C_0) of Rhodamine B at different time catalyzed by NaGdF₄:Yb:Er/Ag/TiO₂ and NaGdF₄:Yb:Er/Ag composites under NIR (980 nm) (b) Terephthalic acid fluorescence spectra at different time catalyzed by NaGdF₄:Yb:Er/Ag/TiO₂ under NIR irradiation



Fig. 9. Rhodamine B degradation spectra with different catalysts (a) NaGdF₄:Yb:Er/TiO₂ (b) NaGdF₄:Yb:Er/Ag, (c) NaGdF₄:Yb:Er/Ag/TiO₂; (d) relative absorbance of Rhodamine B with three different catalyst under UV-visible light irradiation; (e) Rhodamine B structural change with NaGdF₄:Yb:Er/TiO₂ under UVvisible light irradiation.

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Fig. 10. Rhodamine B degradation with NaGdF₄:Yb:Er/Ag/TiO₂ under UV-visible light irradiation from the first to sixth cycles.