



Article Photocatalytic Reactivity of Carbon–Nitrogen– Sulfur-Doped TiO₂ Upconversion Phosphor Composites

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Abstract: Sol–gel synthesized N-doped and carbon–nitrogen–sulfur (CNS)-doped TiO₂ solutions were deposited on upconversion phosphor using a dip coating method. Scanning electron microscopy (SEM) imaging showed that there was a change in the morphology of TiO₂ coated on NaYF₄:Yb,Er from spherical to nanorods caused by additional urea and thiourea doping reagents. Fourier transform infrared (FTIR) spectroscopy further verified the existence of nitrate–hyponitrite, carboxylate, and SO₄^{2–} because of the doping effect. NaYF₄:Yb,Er composites coated with N- and CNS-doped TiO₂ exhibited a slight shift of UV-Vis spectra towards the visible light region. Photodecomposition of methylene blue (MB) was evaluated under 254 nm germicidal lamps and a 300 W Xe lamp with UV/Vis cut off filters. The photodegradation of toluene was evaluated on TiO₂/NaYF₄:Yb,Er and CNS-doped TiO₂/NaYF₄:Yb,Er samples under UV light illumination. The photocatalytic reactivity with CNS-doped TiO₂/NaYF₄:Yb,Er surpassed that of the undoped TiO₂/NaYF₄:Yb,Er for the MB solution and toluene. Photocatalytic activity is increased by CNS doping of TiO₂, which improves light sensitization as a result of band gap narrowing due to impurity sites.

Keywords: CNS-doped TiO₂; NaYF₄:Yb,Er; upconversion phosphor; UV-Vis–NIR photocatalysis

1. Introduction

Titanium dioxide (TiO₂) inorganic semiconductors have emerged as trending materials for photocatalysis applications [1–3]. The band gap of 3.2 eV necessitates ultraviolet (UV) light absorption to cause electron movement from the valence band to the conduction band to progress the photocatalytic reaction. However, these photoreactions only proceed within the UV portion of the solar spectrum, which leaves the broad portions of visible and near infrared (NIR) spectra undetected. Reversing the visible and NIR scattering phenomenon using TiO₂ remains an arduous task for researchers. The methods for improving spectral absorbance include doping with metals and non-metals [4–7] and coupling with other compounds to form nanocomposites [8,9].

Doping TiO₂ with elements such as B [10,11], C, N, and S [12–14] is among the extensively studied techniques used to narrow the band gap. C and N are organic elements that possess remarkable electronic structures and lower toxicity than metallic elements. Thus, non-metallic doping is advantageous because of the smaller ionic radii that can occupy the interstitial sites of TiO₂ [15–17]. The extra energy levels imparted by dopants in TiO₂ promote absorption of visible light photons [18]. To date, several studies have reported alternative mechanisms for electron–hole reaction pathways to facilitate photocatalysis. Specifically, N-doped TiO₂ forms a unique band structure as a substitution at vacancy or interstitial sites in TiO₂. As a result of this, the TiO₂ band gap of 3.2 eV is narrowed to

between 2.8 and 3.06 eV. The doped TiO₂ then sensitizes visible light through the low-energy sites occupied by N for photocatalytic reactions. Consequently, N-doped TiO₂ is reported to perform better in photodegradation reactions due to suppressed electron recombination [16,19]. However, in tri-doped CNS-TiO₂, C, N, and S elements substitute at O sites in TiO₂. In other words, the 2p orbitals of C, N, and S interact with O orbitals inside TiO₂'s conduction band. Therefore, new energy levels from the CNS doping elements lower the overall band structure of TiO₂. The great advantage of multi-element doping is that the sensitization sites increase several times as compared to singly doped element [14,20,21]. However, utilizing N- or CNS-doped TiO₂ nanoparticles in aquatic and air purification methods requires a stable substrate to immobilize and prevent release of TiO₂ into the environment. There are several immobilizing substrates for practical application of TiO₂ nanoparticles, which include stainless steel [22] and glass [23]. However, these substrates only offer support. Their chemical composition has minimal effects in terms of improving the light absorption, which is essential for photocatalytic activity progression. Thus, there is a need to stabilize the nanoparticles in micro-sized compounds such as NaYF₄:Yb,Er phosphors, which possess light-harvesting properties in the NIR region.

Although upconversion phosphors have short photoluminescence lifetimes, if coupled with TiO_2 they promote light harvesting or photocatalysis, even under visible light photons, due to the heterojunction effect [24,25]. The heterojunctions that exist at interfacial peripheries of the TiO_2 catalyst and phosphor support material are associated with modified electronic structure due to defects [24,26]. This phenomenon distinguishes NaYF₄:Yb,Er from other compounds, since both the heterojunctions and the light upconversion effects simultaneously improve the optical and photocatalytic performance of the composites.

Coupling TiO₂ with NaYF₄:Yb,Er phosphor has been reported as a promising approach for utilizing low-energy photons in the NIR region and emitting UV-visible light [27,28]. Over the past decades, NaYF₄:Yb,Er has been utilized to convert NIR 980 nm photons to emitted photons at 525–550 nm [26,29,30], and even at lower wavelengths such as 390–420 nm [31]. However, only the TiO₂ coating on phosphor has been reported to cause improved photocatalytic efficiencies after a long photoreaction time above 10 h [32]. There is a need to evaluate photocatalysis in consideration of the amount of catalyst in the reactor, the light source intensity, and the concentration of pollutant in an effort to complete the photoreaction rapidly. The effect of N doping [33] or carbon–nitrogen–sulfur (CNS) doping [21] has been reported as a method to promote visible light activation of TiO₂, but few studies have been reported that compare the effect of coupling N-doped or CNS-doped TiO₂ with NaYF₄:Yb,Er phosphor.

This study focuses on investigating the effects of N doping and CNS doping of TiO₂ and coupling with NaYF₄:Yb,Er upconversion phosphor. The stability of the organic–inorganic molecular bonding was characterized to confirm the existence of dopants in the TiO₂/NaYF₄:Yb,Er composites. Photocatalytic properties were evaluated with aqueous methylene blue (MB) and toluene pollutant mediums. The photocatalyst samples of N- or CNS-doped TiO₂/NaYF₄:Yb,Er were activated by UV, visible, and NIR light illumination of the solar spectrum.

2. Results

Figure 1 shows XRD spectra of NaYF₄:Yb,Er phosphor composites. The crystallinity is indexed for the phosphor in reference to hexagonal sodium, yttrium, ytterbium, erbium, and fluoride (JCPDS 00–028–1192). The NaYF₄:Yb,Er phosphor peaks were centered at (100), (110), (101), (200), (111), (201), (211), and (311). However, doping elements and TiO₂ crystal were undetectable in the composites owing to the relatively small amounts coated on the sub-micron phosphor matrix. The XRD peaks were invariant in terms of peak broadening, which normally confirms the effect of N or CNS doping in TiO₂.



Figure 1. XRD spectra of (**a**) NaYF₄:Yb,Er phosphor and NaYF₄:Yb,Er coated with (**b**) TiO₂, (**c**) N-TiO₂, and (**d**) CNS-TiO₂.

Figure 2 shows SEM images of NaYF₄:Yb,Er (Figure 2a), TiO₂ (Figure 2b), TiO₂/NaYF₄:Yb,Er (Figure 2c), N-TiO₂/NaYF₄:Yb,Er (Figure 2d), and CNS-TiO₂/NaYF₄:Yb,Er (Figure 2e). The phosphor particles in Figure 2a are in the ~10 micrometer range, while the undoped TiO₂ particles in Figure 2b are agglomerates with a spherical morphology measuring 20–50 nm. Table 1 shows the elemental compositions of F, Na, Y, Er, and Yb. When the TiO₂ sol was coated on the phosphor, its spherical morphology was maintained (Figure 2c). Table 2 shows the elemental compositions of O, F, Na, Ti, Y, Er, and Yb. However, with N and CNS doping in TiO₂, the TiO₂ morphology changed to clustered nanorods on the surfaces of phosphor particles (Figure 2d,e). Table 3 shows the elemental compositions and confirms the presence of N, O, F, Na, Ti, Y, Er, Yb, and the N-doped TiO₂ at 0.17 at.% N. The dense nanorods' TiO₂ morphology is presumed to be because of the change in pH after addition of the urea (N) or thiourea carbon-nitrogen-sulfur (CNS) doping reagent, as described in the Materials section. Table 4 shows the elemental compositions of C, N, O, F, Na, S, Ti, Y, Er, and Yb. The EDS spectra are shown in Figures S1, S3, S5, and S7. The EDS elemental mapping data are shown in Figures S2, S4, S6, and S8. Interestingly, the CNS-doped TiO₂ shows values of C 46.30 at.%, N 0.79 at.%, and 0.15 at.%. Therefore, the thiourea doping reagent is a rich source for CNS elements.



(a)



(b)

Figure 2. Cont.



(c)





(e)

Figure 2. SEM images of (**a**) NaYF₄:Yb,Er, (**b**) TiO₂ particles, and NaYF₄:Yb,Er phosphors coated with (**c**) TiO₂, (**d**) N-TiO₂, and (**e**) CNS-TiO₂.

Element	Mass%	Atom%
F	29.22	60.86
Na	10.19	17.54
Y	35.63	15.86
Er	5.11	1.21
Yb	19.84	4.54

Table 1. Elemental analysis for NaYF_{4:}Yb,Er.

Table 2. Ele	emental a	nalysis fo	or TiO ₂ /Na	aYF4:Yb,Er.
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100

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Totals

Element	Mass%	Atom%
0	4.15	8.98
F	30.85	56.25
Na	10.66	16.05
Ti	4.66	3.37
Y	28.35	11.05
Er	4.42	0.92
Yb	16.91	3.38
Totals	100	-

Element	Mass%	Atom%
Ν	0.07	0.17
0	7.33	16.30
F	25.62	48.01
Na	7.59	11.75
Ti	11.12	8.27
Y	28.43	11.38
Er	4.27	0.91
Yb	15.57	3.20
Totals	100	-

Table 3. Elemental analysis for N-TiO₂/NaYF₄:Yb,Er.

Table 4. Elemental analys	sis for CNS-Ti	O ₂ /NaYF ₄ :Yb,Er.
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Element	Mass%	Atom%
С	25.97	46.30
Ν	0.52	0.79
О	12.79	17.12
F	19.41	21.89
Na	5.41	5.04
S	0.23	0.15
Ti	7.94	3.55
Y	14.60	3.52
Er	2.78	0.36
Yb	10.36	1.28
Totals	100	-

FTIR spectroscopy results for N-TiO₂/NaYF₄:Yb,Er and CNS-TiO₂/NaYF₄:Yb,Er are shown in Figure 3a,b, respectively. The stretching vibrations at 3410 and 1624 cm⁻¹ are assigned to the -OH groups bonded to Ti- atoms and H₂O bending, respectively; while the stretching vibrations at 1369 and 1130 cm⁻¹ arise from carboxylate and S = O bonds, respectively, because of surface-adsorbed SO₄^{2–} species. The stretching vibrations at 1044 and 616 cm⁻¹ are because of hyponitrite and the Ti-O groups, respectively [34].



Figure 3. Fourier transform infrared spectra of NaYF₄:Yb,Er coated with (a) N-TiO₂ and (b) CNS-TiO₂.

Figure 4 exhibits UV-Vis absorption spectra of NaYF₄:Yb,Er coated with undoped, N-doped, and CNS-doped TiO₂. The NaYF₄:Yb,Er phosphor absorbs UV light from 200 nm with an edge at 250 nm (due to the NaYF₄ host), and in Figure S9 absorption peaks were centered at 524 and 654 nm due to the Er^{3+} co-activator [35]. However, coating TiO₂ on phosphor broadened the absorption spectra. Specifically, the TiO₂/NaYF₄:Yb,Er composites exhibited UV-Vis absorption between 200 and 400 nm, with peak absorption at 300 nm. The additional N-doped and CNS-doped TiO₂ phosphor composites

show higher absorption intensities and a slight shift towards the visible region; the red-shift has been referenced by other researchers as being because of the lower energy levels in TiO_2 imparted by N or CNS doping elements [20,36].



Figure 4. UV-Vis absorption spectra of NaYF₄:Yb,Er coated with TiO₂, N-TiO₂, and CNS-TiO₂.

Figure 5a shows photoluminescence (PL) spectra as obtained after 980 nm NIR irradiation of NaYF₄:Yb,Er upconversion phosphor composites. Firstly, the full emission spectra (UV-Vis–NIR emission) in Figure 5a exhibit emissions of visible light photons at 520, 527, 540, and 548 nm. Thus, as a result of simultaneous energy transfer occurring in the excited phosphor, the energy losses resulted in lower energy photons at 652 and 658 nm. The ${}^{2}H_{11/2}$ -to- ${}^{4}I_{15/2}$ transition is assigned to the emission at 527 nm, while the ${}^{4}S_{3/2}$ to ${}^{4}I_{15/2}$ is assigned to the emission at 540 nm. Additionally, the transitions emitting low-energy photons at 652 nm are from ${}^{4}F_{9/2}$ to ${}^{4}I_{15/2}$ [25]. The overall reduction in emission peaks in the TiO₂-coated NaYF₄:Yb,Er samples was also observed in previous research [32]. Thus, TiO₂ nanoparticles on phosphor act as barriers to emitted light.



Figure 5. Photoluminescence spectra of NaYF₄:Yb,Er coated with TiO₂, N-TiO₂ and CNS-TiO₂. (a) UV-Vis–NIR emissions and the enlarged spectra for (b) UV light, (c) visible light, and (d) NIR light emissions.

Figure 5a was enlarged and labeled (Figure 5b–d) to clearly observe peak variations. Figure 5b shows UV light emission at 384 nm and visible light photons at 407 and 484 nm in the NaYF₄:Yb,Er phosphor. However, all of these peaks were suppressed in TiO₂/NaYF₄:Yb,Er and N/CNS-doped TiO₂/NaYF₄:Yb,Er composites. The effect of doping on photoluminescence was observed in the enlarged peaks in Figure 5c,d. Specifically, at 520 and 527 nm in Figure 5c, the TiO₂/NaYF₄:Yb,Er and CNS-doped TiO₂/NaYF₄:Yb,Er show unchanged emission intensities, while only N-doped TiO₂/NaYF₄:Yb,Er exhibits further peak suppression. However, at the peaks located at 540 and 548 nm, the CNS-doped TiO₂/NaYF₄:Yb,Er exhibits the highest photoluminescence, followed by TiO₂/NaYF₄:Yb,Er and N-doped TiO₂/NaYF₄:Yb,Er.

Figure 5d shows the enlarged PL emission spectra to clearly show peaks in the NIR region. At 652 and 658 nm, the peak intensity decreases in the order of NaYF₄:Yb,Er > TiO₂/NaYF₄:Yb,Er TiO₂ > CNS-doped TiO₂/NaYF₄:Yb,Er > N-doped TiO₂/NaYF₄:Yb,Er. The peak suppression and enhancement phenomena represent a multi-energy transfer process. However, some researchers have highlighted that the pH level in urea (the doping reagent in phosphor) tunes the PL emissions for visible and NIR emissions in Y₂O₃:Yb,Er nanophosphors [37]. Thus, in our work we confirmed the tuning of visible and NIR emissions. In the N-doped TiO₂/NaYF₄:Yb,Er (urea additive: pH 5.79) and in CNS-doped TiO₂/NaYF₄:Yb,Er (thiourea additive: pH 5.73) as compared to undoped TiO₂/NaYF₄:Yb,Er (pH 6.39), the pH values are almost the same, however the most acidic CNS-doped phosphor exhibits the highest PL intensity (at 540 and 548 nm), followed by the TiO₂ phosphor and the doped TiO₂-coated samples. Upconversion phosphors are characterized by having short lifetimes, as exhibited in the decay curves in Figure S10.

Figure 6 shows the photobleaching variation of the MB solution for NaYF₄:Yb,Er phosphor composites under UV light illumination. The maximum peak at 664 nm is the characteristic MB absorbance that is monitored to evaluate intensity variations as a measure of the degradation of the organic compound. In a 4 h reaction period, the CNS-TiO₂/NaYF₄:Yb,Er absorbance spectra with the lowest intensities at seen at 4 h. Therefore, CNS-TiO₂/NaYF₄:Yb,Er shows the highest photocatalytic reactivity among the three samples. However, the TiO₂ and N-TiO₂ upconversion phosphor composites require more time to completely degrade MB solutions (Figure 6b,c).



Figure 6. Methylene blue (MB) absorbance variation for NaYF₄:Yb,Er phosphor coated with (**a**) TiO₂, (**b**) N-TiO₂, and (**c**) CNS-TiO₂ under UV light activation.

Figure 7a shows the peak absorbance variations for photodegradation of the MB solution under UV illumination. The photodegradation of the MB solution proceeded to 40% efficiency for the photoreaction mixture with TiO₂ only. However, N-doped TiO₂ and CNS-doped TiO₂ improves the efficiency to 80%. This is owing to the light absorption property related to N- and CNS-doped TiO₂. Supporting TiO₂ on the NaYF₄:Yb,Er upconversion phosphor improved the photocatalytic efficiency up to 90%. Moreover, with N-TiO₂ or CNS-TiO₂ supported on NaYF₄:Yb,Er, the photocatalytic efficiencies were enhanced to completion (100% in 4 h). Thus, N-TiO₂ or CNS-TiO₂ coupling with NaYF₄:Yb,Er phosphor improves the catalytic activity due to the improvement in light absorption by phosphor and N or CNS doping elements. In detail, the NaYF₄:Yb,Er phosphor support has light absorption properties due to the NaYF₄ host (as exhibited in Figure 4), which coincides with the TiO₂ absorption band. Additionally, light absorption for the composite is improved with additional N and CNS doping.



Figure 7. (**a**) MB peak absorbance variation as degraded with 254 nm UV illumination. Here, UP is the NaYF₄:Yb,Er upconversion phosphor and (**b**) correlated rate of kinetics.

Both CNS doping and N doping of TiO₂ further cause improvements in photocatalytic efficiencies. The N or CNS doping of TiO₂ incorporates new energy levels in the interstitial and substitution sites. Thus, lower energy levels lower the TiO₂ absorption band, which promotes the flow of electrons into the conduction band. As follows, the photocatalytic activity achieves completion in a 4 h cycle for phosphor coated with doped CNS or N-TiO₂. Figure 7b illustrates the rate of kinetics for the samples in Figure 7a. As shown in Figure 7b, the reactions have a linear and typical relationship for first-order kinetics. The rate constants are 0.16 min⁻¹ for TiO₂, 0.37 min⁻¹ for N-TiO₂, 0.41 min⁻¹ for CNS-TiO₂, 0.0072 min⁻¹ for NaYF₄:Yb,Er, 0.58 min⁻¹ for TiO₂/NaYF₄:Yb,Er, 0.91 min⁻¹ for N-TiO₂/NaYF₄:Yb,Er, and 1.2 min⁻¹ for CNS-TiO₂/NaYF₄:Yb,Er. This result shows that MB photodegradation with CNS-TiO₂/NaYF₄:Yb,Er is the fastest reaction by 7.5 times for TiO₂, by 3.2 times for N-TiO₂, by 2.9 times for CNS-TiO₂, by 2.1 times for TiO₂/NaYF₄:Yb,Er, and by 1.3 times for N-TiO₂/NaYF₄:Yb,Er. Therefore, CNS doping of TiO₂ and its support on NaYF₄:Yb,Er phosphor improves the photocatalytic performances.

Figure 8 exhibits the MB peak absorbance against time for visible light activation. The N-doped TiO₂ and CNS-doped TiO₂ show improvements in visible light photocatalytic efficiencies as compared to TiO₂ only. Furthermore, coupling TiO₂ with phosphor and doping the TiO₂/NaYF₄:Yb,Er causes enhancements of photocatalytic efficiencies. Precisely, TiO₂/NaYF₄:Yb,Er, N-doped TiO₂/NaYF₄:Yb,Er and CNS-doped TiO₂/NaYF₄:Yb,Er showed 50%, 60%, and 70% efficiencies after 120 min of light irradiation. The undoped TiO₂/NaYF₄:Yb,Er composite showed significant photocatalytic efficiency as compared to TiO₂, N-TiO₂, and CNS-TiO₂, mainly due to the heterojunction effect that exists between phosphor and TiO₂. The CNS-doped TiO₂/NaYF₄:Yb,Er shows the highest photocatalytic reactivity over visible light illumination. As a result, the effect of doping with N-TiO₂/NaYF₄:Yb,Er or CNS-TiO₂/NaYF₄:Yb,Er is clearly exhibited by 10% and 20% efficiency enhancements, respectively, compared with undoped-TiO₂/NaYF₄:Yb,Er. Visible light sensitization is conceptualized by the low-energy states induced by doping with N or CNS elements. Thus, tri-element doping in TiO₂ imparts more impurities in the TiO₂ band than N doping only. Figure 8b shows the rate of kinetics for the samples

in Figure 8a. The CNS-doped TiO₂/NaYF₄:Yb,Er exhibited the swiftest reaction with a 9.7×10^{-3} min⁻¹ rate constant. In comparison with other photocatalysts, the CNS-doped TiO₂/NaYF₄:Yb,Er reaction is 9.7 times greater for TiO₂ only, 4.4 times greater for N-TiO₂, 2.8 times greater for CNS-TiO₂, 1.8 times greater for TiO₂/NaYF₄:Yb,Er, and 1.2 times greater for N-TiO₂/NaYF₄:Yb,Er. Therefore, the photocatalytic efficiencies are improved by tri-doping TiO₂ and its support on the NaYF₄:Yb,Er upconversion phosphor.



Figure 8. (a) MB peak absorbance against the visible light activation time and (b) correlated rate of kinetics.

Figure 9 shows the MB peak absorbance against time for NIR light activation. Undoped TiO₂-phosphor and N-doped TiO₂-phosphor composites only show ~15% efficiency with NIR illuminations, but CNS-doped TiO₂/NaYF₄:Yb,Er exhibits a ~25% improvement. Therefore, NIR irradiations in CNS-doped TiO₂/NaYF₄:Yb,Er have the highest photocatalytic activity. Under NIR, the Yb³⁺ in NaYF₄:Yb,Er phosphor sensitizes the NIR photons and emits UV-Vis–NIR photons through the Er^{3+} emission center, as discussed in Figure 5. Visible light photons are sensitized through the low energy levels imparted by N- or CNS doping and electrons are injected into the TiO₂ conduction band for photocatalysis. Additionally, the doping elements promote electron–hole generation efficiencies to facilitate photocatalysis. However, the overall photocatalytic efficiencies were low due to the mono-wavelength absorption properties of Yb³⁺ ions at 980 nm.



Figure 9. (a) MB peak absorbance against the NIR light activation time and (b) correlated rate of kinetics.

Figure 10 exhibits the concentration variations of toluene during photodegradation with TiO_2 -NaYF₄:Yb,Er and CNS/TiO₂-NaYF₄:Yb,Er powders under UV light illumination. The toluene concentration in the Y-axis corresponds to the concentration of toluene remaining in the Teflon bag after 1 h sampling under UV light illumination. Through the first 1 h sampling cycle, the CNS/TiO₂-NaYF₄:Yb,Er photocatalyst has 1.5 ppm of toluene less than the undoped TiO₂-NaYF₄:Yb,Er sample. The 4 h toluene degradation is above 95% for the CNS/TiO₂-NaYF₄:Yb,Er.

This result indicates that the CNS/TiO₂-NaYF₄:Yb,Er has exceptionally superior photoactivity compared with the TiO₂-NaYF₄:Yb,Er sample. Thus, CNS doping is essential for improving photocatalytic activity.



Figure 10. Photodegradation for toluene with CNS-TiO₂/NaYF₄:Yb,Er and TiO₂/NaYF₄:Yb,Er composites under UV light illumination.

3. Discussions

Figure 11 is a schematic diagram depicting the synthesis and photocatalytic test performances. The pH of the coating sol varied due to the interaction of the TiO_2 precursor and ethanol without pH modifiers. Thus, the TiO_2 sol without the doping reagent showed slightly alkaline conditions at pH 6.39. As a result of this slight alkalinity, the TiO_2 morphology existed as spherical particles on phosphor. However, with additional thiourea and urea as doping reagents for N and CNS in the TiO_2 sol, the pH decreased to acidic conditions. For instance, in the N-doped TiO_2 sol the pH was 5.79, while in the CNS-doped TiO_2 sol the pH was 5.73. As a result, the morphologies were changed to nanorods. Hence, the drop in pH promoted the formation of nanorods. The photoluminescence emission peaks were also observed to be tuned by urea or thiourea reagents owing to the drop in pH.



Figure 11. Schematic diagram for synthesis and photocatalysis tests.

Figure 12 shows the proposed photocatalysis mechanism for the $NaYF_4$:Yb,Er phosphor coated with TiO₂ under different doping conditions. The three conditions for TiO₂ coating on NaYF₄:Yb,Er

are illustrated in Figure 12 as TiO₂, N-TiO₂, and CNS-TiO₂. The first condition is TiO₂ supported on NaYF₄:Yb,Er phosphor, where only the TiO₂ energy band is present. The second condition is N-doped TiO₂ supported on NaYF₄:Yb,Er, where the continuous solid line inside the TiO₂ represents N energy levels. The third condition is CNS-doped TiO₂ supported on NaYF₄:Yb,Er, where the dotted line in the TiO₂ band represents discrete energy levels imparted by C, N, or S elements. As illustrated, the upconversion phosphor as the support material contains Yb³⁺ as the NIR sensitizer in the ²F_{7/2} state, which transfers energy to the co-activator or Er³⁺ through the ⁴F_{7/2} and ⁴I_{11/2} states [35,38,39]. Simultaneously, the Er³⁺ emits UV-Vis–NIR photons of less than 980 nm. Hence, the upconversion phosphor converts low-energy NIR photons at 980 nm to high-energy photons (Figure 5). Peak wavelengths were observed at 384, 407, 520, 527, 540, 548, 652, 658, and 836 nm. Thus, NaYF₄:Yb,Er upconversion phosphor emits UV-Vis–NIR photons.



Figure 12. Proposed photocatalysis mechanism for the NaYF₄:Yb,Er phosphor coated with TiO₂ under different doping conditions.

Photocatalytic activity proceeds under UV-Vis-NIR irradiation. The reactions are related to light sensitization centers [40]. For instance, under UV light activation, the TiO₂-NaYF₄:Yb,Er composite absorbs light and facilitates photocatalysis. It is noteworthy that the NaYF₄ phosphor host also sensitizes UV light photons (Figure 4), which enhances the overall light absorption by the TiO₂-NaYF₄:Yb,Er composite. Under visible light, N-TiO₂-NaYF₄:Yb,Er or CNS-TiO₂/NaYF₄:Yb,Er light is sensitized through the lower energy levels in the N or CNS, which inject electrons into the TiO₂ conduction band for photoreaction at the nanorod surface. Under NIR irradiation, the light is sensitized through the Yb³⁺ and energy is transferred through Er^{3+} . Then, the emitted visible light is absorbed through low-energy impurities in N or CNS elements and through the low energy levels due to heterojunctions between TiO₂ and NaYF₄:Yb,Er phosphor. Consequently, after sensitization of UV-Vis–NIR light, electrons are injected into the TiO₂ conduction band, leaving holes in the valence band. At the surface of TiO₂, electrons are adsorbed by O₂ molecules while holes are adsorbed by H₂O molecules to form superoxide and hydroxyl radicals, respectively. After several intermediate reactions, superoxide or hydroxyl radicals attack and photodegrade the MB or toluene pollutants. The CNS-doped $TiO_2/NaYF_4$:Yb,Er outperformed the N-doped TiO₂-NaYF₄:Yb,Er and TiO₂-NaYF₄:Yb,Er in UV-Vis–NIR photocatalytic activities in methylene blue due to the existence of low-energy CNS doping elements with improved light absorption properties [20].

This work mainly focused on adding 2.5% urea or thiourea to TiO₂ to study the effects of doping with N or CNS. Since the photoluminescence spectra exhibited interesting visible and NIR light tuning, further investigations into the effects of varying urea or thiourea (N or CNS, respectively) doping of TiO₂/NaYF₄:Yb,Er is recommended. Specifically, the photoluminescence emissions at 540 and 548 nm in CNS-doped TiO₂/NaYF₄:Yb,Er were enhanced (Figure 5b) compared to the TiO₂-NaYF₄:Yb,Er and N-TiO₂-NaYF₄:Yb,Er. This insinuates the possibility that CNS doping improves the emission of visible

light. Additionally, the photoluminescence under NIR is limited due to the narrow absorption of Yb^{3+} ions to the 980 nm wavelengths [39,40]. It is also recommended to evaluate the effects of adding 2 co-sensitizers to improve the absorption of NIR light to achieve significant photocatalytic efficiency.

4. Materials and Methods

4.1. Experimental

The NaYF₄:Yb,Er upconversion phosphor was synthesized from a stoichiometric amount of Y:Yb:Er at 77:20:3 mol% from yttrium, ytterbium, and erbium oxides (99.9%, Sigma Aldrich, St. Louis, MO, USA) by mixing in a nitric acid solution. The mixture solution was constantly stirred at 120 °C for 30 min to form a transparent sol. In a separate beaker, urea, ammonium hydrogen fluoride, and sodium silicon fluoride (Duksan Pure Chemicals Co., Ansan-si, Kyunggi-do, Korea) were dissolved in distilled H₂O by magnetic stirring at 80 °C for 2 h. Then, the multi-component NaYF₄:Yb,Er solution was poured into a closed crucible for combustion at 650 °C for 5 min in a box furnace (SK1700-B30, Thermotechno Co., Siheung-si, Gyeonggi-do, Korea).

A flow chart of the TiO₂ sol preparation and coating process on NaYF₄:Yb,Er is shown in Figure 13. The TiO₂ sols were prepared from 10 mL titanium(IV)-butylate (99%, Acros Organics) with anhydrous ethyl alcohol (99.9%, Duksan Pure Chemicals Co., Ansan-si, Kyunggi-do, Korea) and distilled H₂O at a volumetric ratio of 5:1. After a 10 min mixing procedure, the 2.5 mol% urea or 2.5 mol% thiourea doping reagents (Daejung Chemicals Siheung-si, Gyeonggi-do, Korea) for N or CNS were added to separate beakers with TiO₂ sol. The N- or CNS-doped TiO₂ sols were further magnetically stirred at 50 °C for 2 h. For comparison, undoped TiO₂ sol was also prepared using similar conditions. The pH for the as-synthesized coating solutions was measured using a Hanna Instruments portable digital meter (HI 8424, Smithfield, RI, USA). The pH readings for the TiO₂ sol, N-doped TiO₂ sol, and CNS-doped TiO₂ sol were 6.39, 5.79, and 5.73, respectively. Thus, the pH values dropped with urea and thiourea reagents.



Figure 13. Flow chart of TiO₂ sol preparation and its coating process on NaYF₄:Yb,Er.

The sol-gel coating process was proceeded by dip coating 2 g NaYF₄:Yb,Er upconversion phosphor powder samples in 5 mL of TiO₂ sol, N-TiO₂ sol, or CNS-TiO₂ sol. The dispersed NaYF₄:Yb,Er phosphor was treated in an ultrasonic bath for 5 min followed by removal of excess ethanol solution through Advantec filter paper (Toyo Roshi Kaisha, Ltd., Tokyo, Japan). Then, the coated phosphors were placed on a quartz petri dish for drying at 100 °C for 10 h. Finally, the undoped TiO₂, N-doped TiO₂, and CNS-doped-TiO₂ coated NaYF₄:Yb,Er samples were placed in alumina crucibles with lids for a 2 h calcination process at 450 °C. Only N-doped TiO₂ and CNS-doped TiO₂ were also calcined using a similar process for the purpose of acting as photocatalytic test controls.

4.2. Characterizations

Crystallinity and morphology were evaluated by X-ray diffractometry (Bruker AXS8 Advanced, D8 Discover, Bruker AXS GmbH, Karlsruhe, Germany) and scanning electron microscopy (SEM, Hitachi S-4300, Hitachi Ltd., Tokyo, Japan). The organic and inorganic molecular bonds were examined by Fourier transform infrared (FTIR; Bruker Vertex 70, Karlsruhe, Germany) spectroscopy at a 50:1 wt.% ratio of KBr/phosphor. UV-Vis diffuse reflectance spectra (DRS) for the synthesized composites were evaluated by UV-Vis–NIR spectroscopy (UV-3150 Shimadzu, Kyoto, Japan) in fast scan speed mode through a 30 nm slit. Photoluminescence (PL) characteristics were examined using a fluorescence spectrophotometer (Hitachi F-4500, Tokyo, Japan). The PL powder samples were excited with a 40 mW, 980 nm infrared dot laser (ILaser Lab Co. Ltd., Seong Dong-gu, Seoul, Korea), and the emitted photons were detected through a 10 nm slit.

Photocatalytic activity was evaluated under three conditions of light illumination. First, UV light from 254 nm photons (G6T5 Sankyo Denki 2-fluorescent lamps, Sankyo Denki Co, Kanagawa, Japan) in a protective chamber was illuminated over a mixture of 100 mg catalyst and 100 mL MB 5 ppm solution. Photodegraded 2 mL samples were collected and labeled with respective light irradiation times throughout the 3 light illumination conditions. Second, visible light (10,000 lux, 300 W Xe Solar Simulators Luzchem SolSim2) was irradiated over a 410 nm cut-off filter to the 100 mg catalyst in 50 mL MB 5 ppm solution. Third, NIR photons (15,000 lux, Luzchem SolSim2, Ottawa, Ontario, Canada) were illuminated on a photoreaction of 100 mg catalyst–50 mL MB 2 ppm solution with 410 and 760 nm cut-off filters. The absorbance variation of UV-Vis–NIR photodegraded MB solutions was analyzed in quartz cell holders of a UV-Vis–NIR spectroscope (UV-3150 Shimadzu, Kyoto, Japan). Photocatalytic activity control experiments were also conducted on N-doped TiO₂ only and CNS-doped TiO₂ using the same UV and visible light conditions.

Toluene photodegradation was evaluated on 6 g TiO₂-NaYF₄:Yb,Er and CNS/TiO₂-NaYF₄:Yb,Er powders. The photocatalytic powders were sparsely dispersed on a borosilicate Petri dish in a Teflon sampling bag. The light illumination source was an 8 W Philips TUV G6T5. At 1 h intervals, 1 mL toluene vapor was withdrawn from the sampling bag and injected into an Agilent Technologies gas chromatography (GC) system (7890 A, Agilent Technologies Inc., California, USA) to determine the extent of degradation in relation to the UV light illumination time.

5. Conclusions

Upconversion phosphor was coupled with undoped TiO₂ and N- and CNS-doped TiO₂ using a sol–gel coating method. The TiO₂ nanocrystalline morphologies on NaYF₄:Yb,Er upconversion phosphor changed from spherical to nanorods, most probably due to the use of urea and thiourea doping reagents. N doping and CNS doping in TiO₂ were successful, as confirmed by EDS and FTIR through broad molecular bonds of SO₄^{2–}, carboxylate, and NO₃[–]. The UV-Vis DRS of the photocatalyst powder samples exhibited a slight red-shift with N doping and CNS doping. The MB photocatalytic degradation efficiencies under UV-Vis–NIR illumination sources are enhanced with doping with N or CNS elements. Specifically, N-TiO₂ and CNS-TiO₂ photocatalysts exhibited lower UV-Vis photocatalytic efficiencies as compared to the N-TiO₂ and CNS-TiO₂ supported on NaYF₄:Yb,Er phosphor. Moreover, toluene degradation efficiencies were improved by CNS doping on TiO₂/NaYF₄:Yb,Er. The CNS-doped-TiO₂/NaYF₄:Yb,Er photocatalyst is a plausible candidate for pollutant remediation.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/10/1188/s1, Figure S1: Elemental mapping for NaYF₄:Yb,Er, Figure S2: Elemental spectra for NaYF₄:Yb,Er, Figure S3: Elemental mapping for TiO₂/NaYF₄:Yb,Er, Figure S4: Elemental spectra for TiO₂/NaYF₄:Yb,Er, Figure S5: Elemental mapping for N-TiO₂/NaYF₄:Yb,Er, Figure S6: Elemental spectra for N-TiO₂/NaYF₄:Yb,Er, Figure S7: Elemental mapping for CNS-TiO₂/NaYF₄:Yb,Er, Figure S8: Elemental spectra for CNS-TiO₂/NaYF₄:Yb,Er, Figure S9: UV-Vis absorption spectra enlarged along the absorbance axis from Figure 4, Figure S10: Decay curve for NaYF₄:Yb,Er coated with TiO₂, N-TiO₂ and CNS-TiO₂ monitored at 540 nm under 980 nm excitation.

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