

# The Effect of the Metal Type on Luminescence and Photocatalytic Properties of Lanthanide–Organic Frameworks–Modified Titania <sup>†</sup>

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**Abstract:** A series of lanthanide–naphthalenedicarboxylates–modified TiO<sub>2</sub> (Ln(NDC)–TiO<sub>2</sub>) photocatalysts were prepared via simple hydrothermal method using Tm, Er, Nd, Ho, Eu, Tb, Yb, or La as metal and 2,6-naphthalenedicarboxylic acid as ligand. The photocatalysts were characterized by diffuse reflectance spectroscopy (DRS), photoluminescence spectroscopy (PL), and scanning electron microscopy (SEM). The photocatalytic properties were investigated by employing the photodegradation of phenol in the aqueous phase as a model pollutant. To provide insight into the reactive individuals participating in the degradation mechanism, a test with scavengers was also performed.

**Keywords:** titanium dioxide; lanthanide; metal–organic frameworks; photocatalyst

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## 1. Introduction

Lanthanide (Ln) has become of current interest due to its unique luminescence properties, namely its large anti-Stokes shift, sharp emission band, and long excited–state lifetime. Moreover, lanthanide ions in metal–organic frameworks, in view of their upconverting ability, are promising candidates as modifiers of semiconductor photocatalysts for developing visible light active photocatalysts. Up–conversion luminescence is a nonlinear optical process that involves the conversion of low energy photons into higher energy photons. Trivalent Ln<sup>3+</sup> ions are excellent activators because they have adequate intermediate energy states for energy transfer up–conversion (ETU), which is considered the most efficient mechanism for energy transfer and photon up–conversion [1–3]. Application of solar light to drive pollutant degradation over photocatalysts' surface is one of the green approaches proposed for air, water, and wastewater treatment. Thus, a lot of attention is paid to different methodologies to improve TiO<sub>2</sub> properties in the visible range of the electromagnetic spectrum, because it allows for the obtainment of photocatalysts that are active under solar light. Therefore, the aim of this work was to understand the effect of the 2,6-naphthalenedicarboxylate ligand and types of lanthanide ions (Ln<sup>3+</sup> = Tm, Er, Nd, Ho, Eu, Tb, Yb, La) on luminescence and optical properties, and their relationship with the photocatalytic performance of titanium dioxide in a range of visible radiation.

## 2. Materials and Methods

### 2.1. Synthesis of Photocatalysts

Photocatalysts were prepared via simple hydrothermal method using  $\text{Ln}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  ( $\text{Ln} = \text{Tm}, \text{Er}, \text{Nd}, \text{Ho}, \text{Eu}, \text{Tb}, \text{Yb}, \text{or La}$ ) as the metal precursor and 2,6-naphthenedicarboxylic acid as the ligand precursor. The reactions were carried out in a Teflon-lined autoclave at 120 °C for 72 h. The concentration of metal precursors and 2,6-naphthalenedicarboxylic (2,6-NDC) acid, which amounted to 0.25 mol%, were related to the concentration of titanium precursor (titanium isopropoxide).

### 2.2. Photocatalytic Tests

Photocatalytic activity was evaluated by degradation of phenol under visible light using a 1000 W Xenon lamp (Oriel 66021) equipped with an optical filter (GG420) and a water IR cut-off filter. Experiments were performed in a reactor at initial phenol and photocatalyst concentrations of 0.21 mM and 5 g/L, respectively. Phenol solution samples of 0.5 mL were taken at specific time intervals, filtered using a 0.2  $\mu\text{m}$  syringe filter, and then analyzed. A high-performance liquid chromatograph (HPLC, Shimadzu) equipped with a Kinetex C18 column and a SPD-M20A diode array detector ( $k = 205 \text{ nm}$ ) was used to determine the phenol concentration in the solution. The mobile phase was composed of acetonitrile and 0.005% trifluoroacetic acid using isocratic elution (20/80 v/v), with a constant flow rate equal to 0.4 mL/min. The injection volume was 20  $\mu\text{L}$ .

## 3. Results

Modification of titania with  $\text{Ln}(\text{NDC})$  greatly affected the light absorption property of the photocatalysts. The  $\text{Ln}(\text{NDC})$ -modified  $\text{TiO}_2$  ( $\text{Ln}(\text{NDC})$ - $\text{TiO}_2$ ) samples showed a red shifted at the absorbance edge compared to the reference sample. In addition, the characteristic absorption peaks belonging to  $\text{Ln}^{3+}$  in the visible region were observed. PL spectroscopy revealed that the modified photocatalysts caused a decrease in PL intensity. This indicates that modification effectively inhibits the recombination of electron-hole pairs. SEM images showed porous structures.

### Photocatalytic Activity

Modification of  $\text{TiO}_2$  with  $\text{Ln}(\text{NDC})$  enhanced its photocatalytic activity. All  $\text{Ln}(\text{NDC})$ - $\text{TiO}_2$  photocatalysts exhibited much enhanced photocatalytic activity in degradation of phenol under visible ( $\lambda > 420 \text{ nm}$ ) light irradiation, than bare  $\text{TiO}_2$ . After 60 min of irradiation, 61% of phenol degraded in the presence of the sample containing holmium. It should be noted that the most photoactive sample exhibited the highest initial reaction rate (calculated for the first 20 min of irradiation; see Table 1). In addition, this sample showed stability in four measurement cycles. The influence of the addition of different scavengers on the degradation efficiency of phenol by  $\text{Ln}(\text{NDC})$ - $\text{TiO}_2$  illustrated that electrons, holes, and hydroxyl radicals play important roles in the photocatalytic reaction.

**Table 1.** Description and photocatalytic activity of  $\text{Ln}(\text{NDC})$ - $\text{TiO}_2$  photocatalysts.

Sample Label	Type of Metal Modification	Initial Phenol Degradation Rate under Vis Irradiation ( $\mu\text{mol} \cdot \text{dm}^{-3} \cdot \text{min}^{-1}$ )
Pristine $\text{TiO}_2$	None	$0.35 \pm 0.02$
(Tm(NDC))- $\text{TiO}_2$	Thulium	$4.02 \pm 0.04$
(Er(NDC))- $\text{TiO}_2$	Erbium	$4.65 \pm 0.12$
(Nd(NDC))- $\text{TiO}_2$	Neodymium	$4.20 \pm 0.11$
(Ho(NDC))- $\text{TiO}_2$	Holmium	$4.97 \pm 0.08$
(Eu(NDC))- $\text{TiO}_2$	Europium	$3.30 \pm 0.04$
(Tb(NDC))- $\text{TiO}_2$	Terbium	$3.22 \pm 0.09$
(Yb(NDC))- $\text{TiO}_2$	Ytterbium	$3.39 \pm 0.15$
(La(NDC))- $\text{TiO}_2$	Lanthanum	$2.40 \pm 0.12$

#### 4. Conclusions

The presence of Ln-organic frameworks in the samples influenced the changes in UV–Vis absorption spectra, probably because of the presence of new states in the band gap, which produces a new photonic absorption process and shows photoluminescence properties. The prepared Ln(NDC)–TiO<sub>2</sub> samples can achieve photocatalytic degradation of phenol under visible light ( $\lambda > 420$  nm). The titanium–phenolate bond is known to induce ligand-to-metal charge transfer, thus enhancing light absorption within the visible region. The enhanced photoactivity of Ln(NDC)–modified TiO<sub>2</sub> should result from the visible-light harvesting and the photoinduced charge transfer by Ln modification.

**Author Contributions:** P.P. conceived and designed the experiments; A.Z.-M. was involved in supervised the work; P.P. performed the experiments and analyzed the data; P.P and A.Z.-M. contributed reagents/materials/analysis tools; P.P. wrote the paper.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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