Lanthanide organic frameworks@TiO₂ nanomaterials: luminescence and highly efficient photodegradation of phenol

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Introduction

Over the past few years, the properties of upconverting nanomaterials have been investigated very intensively because of their potential applications in the fields of nanotechnology, nanomedicine, and photovoltaics. In particular, lanthanide-organic frameworks (LnOFs) have become current interests due to their unique luminescence properties, namely large anti-Stokes shift, sharp emission band, and long excited-state lifetime (Cui, Zhang, Chen, & Qian, 2016). These attributes are particularly needed for developing visible light-driven photocatalytic activity of titanium dioxide (TiO₂) (Parnicka et al., 2017). Semiconductor-based heterogeneous photocatalysis is a promising technology for water purification without using consumables and generating harmful by-products.

Materials and Methods

The obtained samples were characterized by diffuse reflectance spectroscopy (Shimadzu UV-Vis Spectrophotometer UV 2600), scanning electron microscopy (JSM-7610F, JEOL) and photoluminescence spectroscopy (LS-50B Luminescence Spectrometer). The photocatalytic activity of the prepared samples was evaluated by photodegradation of phenol in aqueous solution under visible light ($\lambda > 420$ nm) irradiation.

Results

In the first stage, a series of lanthanide-organic frameworks have been hydrothermal synthesized using europium and terbium as metals and carboxylate-based ligands. Thereafter, LnOF@TiO₂ nanocomposites were obtained via surface impregnation technique. A description of the prepared photocatalysts is shown in Table 1.

Table 1. Sample label, preparation conditions and phenol photodegradation of LnOF@TiO₂.

Sample label	Type of metal	Efficiency of phenol photodegradation (%) after 60 min ($\lambda > 420$ nm)
TiO ₂	none	4.2
LnOF(1)@TiO ₂	Eu	11.57
LnOF(2)@TiO ₂	Tb	25.92
LnOF(3)@TiO ₂	Eu	18.30
LnOF(4)@TiO ₂	Tb	9.75
LnOF(5)@TiO ₂	Eu	16.10
LnOF(6)@TiO ₂	Tb	8.12
LnOF(7)@TiO ₂	Eu + Tb (0.2 : 0.8 wt.%)	17.32
LnOF(8)@TiO ₂	Eu + Tb (0.1 : 0.9 wt.%)	9.78

Discussion

The diffuse reflectance spectroscopy (Fig. 1) showed that each photocatalyst has broad intense absorption below 390 nm, which can be assigned to charge-transfer associated with electron excitation from the valence band to the conduction band in TiO₂. Pristine TiO₂ did not exhibit any absorption in the Vis region. All LnOF-modified samples showed a shift of the absorption curve towards the wavelength of a higher value (redshift) compared to that of pristine TiO₂.

Figure 1. UV-Vis DRS spectra of pristine TiO₂ and LnOF@TiO₂ nanocomposites.

Photoluminescence (PL) properties presented a weak broad emission band with a maximum intensity at around 350-600 nm. It can be seen that LnOF modification of TiO₂ did not induced new luminescence phenomenon but affects only the PL intensity signal. After modification, it observed an increase in intensity compared to that of pristine TiO₂. LnOF induces an increase in various phenomena such as phonon transition, charge transfer, and surface oxygen defects. The composite photocatalysts exhibit much enhanced photocatalytic activity in degradation of phenol under visible light irradiation, with is 6 times higher than that of pristine TiO₂. The highest degradation was observed for LnOF(2)@TiO₂ sample, with the efficiency reached 25.9% after 60 min. The enhanced activity is probably attributed to: (1) the presence of new states in the band gap, which products a new states in the band gap, (2) the effective separation of charge carries and (3) energy transfer from LnOF to TiO₂ (Mazierski et al., 2018). Such a composite photocatalyst is promising for water purification application and environmental remediation.

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