Chapter

Rare-Earth-Based Materials for Heterogeneous Photocatalysis

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Abstract

Recently, the synthesis of rare-earth-based nanostructures as a significant class of materials with photocatalysis activity has attracted the attention of researchers. Many studies have shown their applications in various fields, specifically in photocatalysis. There are different methods to synthesis of rare-earth nanostructures. In this study, we discuss about modification of rare-earth-based materials. Also production methods and their advantages and disadvantages have been presented, briefly. Finally, photocatalytic applications of rare-earth nanostructures are highlighted.

Keywords: rare-earth materials, heterogeneous photocatalysis, nanostructure, methods, modification

1. Introduction

Nanostructures especially rare-earth-based materials have attracted interest of researches in recent decade due to their unique and important properties such as electronic, optical, photocatalytic and magnetic. These materials with different shapes can be used in various fields because of potential applications. Because their dimension and shape the behavior of nanoscale compounds is greatly sensitive [1].

A set of chemical elements in the periodic table, specifically scandium (Sc), yttrium (Y), lanthanum (La) and all of the lanthanide series (Ln), are rare-earth materials. All rare-earth materials have unique properties corresponding to the filling of their orbitals and their ability to display a 3+ oxidation state [2, 3]. The results of researchers show that rare-earth material properties changes with doping or co-doping of them with oxides because of their crystalline structure variation.

Rare-earth-based materials were generally applied in high and low temperature fuel cells [4], gas storage/separation, chemical sensing [5], heterogeneous photocatalysis [6], wastewater treatment [7], fluorescence [8], photoelectrochemical Water [9], etc. Nanostructure of rare-earth material is appropriate for these applications that can be synthesized with different methods for example coprecipitation, hydrothermal, sol-gel, combustion, stearic acid route, pechini, cathode plasma, electrolysis, co-ions complexation, molten salt and other approaches [7]. Each of these methods has its own advantages and disadvantages which are discussed in the following.

This study is being focused on heterogeneous photocatalytic activity of rare-earth-based material and their methods of preparation.

2. Modification of rare-earth-based materials

Efficiency of nanostructured compounds depend their grain size, morphology, structure and components. Study on properties of rare-earth oxide and doped with other material has increased due to their wide usages in various fields [10]. In order to develop properties, excessive effort has been done in the modification of morphology and structure of rare-earth materials.

Praseodymium oxide (Pr_6O_{11}), neodymium oxide (Nd_2O_3), holmium oxide (Ho_2O_3), $Dy_2Ce_2O_7$, $Nd_2Zr_2O_7$-Nd_2O_3, NdOCl-$Nd_2Sn_2O_7$-SnO_2, $Nd_2Sn_2O_7$-SnO_2, $Pr_2Ce_2O_7$, $Nd_2Sn_2O_7$, $Nd_2Zr_2O_7$-ZrO_2, $Nd_2Zr_2O_7$, $Dy_2Sn_2O_7$-SnO_2, Ho_2O_3-SiO_2, Nd_2O_3-SiO_2, are various families of rare-earth-based materials that were synthesized by researchers [10–20] to modify their properties and other modified rare-earth materials will be presented in the following.

2.1 Rare-earth-based coordination polymers

Rare-earth-based coordination polymers (CPs) have been studied due to their expanded structures and applications [5]. These materials contain catalytic active sites in both the organic linkers and metal centers. The modified of new and selective heterogeneous catalysts is suitable for photocatalytic processes, mainly in the oxidation of organic compounds.

Aguirre-Díaz et al. [5] synthesized five new lanthanide CPs (Ln-CPs) by solvothermal method using La, Nd, Sm, Ho, and Er as metal sources in order to offer a remarkable platform which contains antennas and catalytic active centers to achieve solar-energy conversion as green alternatives.

Also Le Natur et al. [21] synthesized a series of hexanuclear complexes based coordination polymers (CPs). They showed that CPs contain rare-earth material exhibit very high optical, luminescent properties and tunable systems at low cost. Therefore they demonstrated that this modified materials had high photocatalytic activity.

2.2 Rare-earth-based metal organic frameworks

Metal organic frameworks (MOFs) are crystalline porous materials with bridging organic ligands, which inorganic metal place in center. Nevertheless, applications of MOFs were limited because of their weak coordination capability and the stability. To solve this problem, Feng et al. [22] synthesized stable and functional 8-connected hexanuclear rare-earth MOFs platform based on $Re_6O_4(OH)_4(COO)_8$ Clusters. They showed that these structural characteristics cause that MOFs perform as a multipurpose platform for future applications, including recognition and high adsorption.

3. Methods for preparing rare-earth-based nanostructures

Shape of material as well as dimension will be influenced by the preparation method of nanoscale compounds. Therefor selection of technique is essential to control the shape of nanostructure [7]. In this section, we study some of methods for preparing rare-earth-based nanostructures.

3.1 Solid state reaction

In the solid state reaction as conventional method for synthesis, rare-earth oxide and other material are mixed using mechanical instrument and the achieved powders are calcined at very high temperature for very long time [23].

Eu^{3+} doped $Gd_2Mo_3O_9$ was prepared using solid-state reaction method and Na_2C0_3 as flux by Xiaoxia [24]. The results showed that the luminescent and photocatalytic properties depend to flux content and sintering temperature.

3.2 Hydrothermal

In the hydrothermal method, materials solutions are placed in the autoclave under high temperature and pressure conditions therefore the hydroxides are precipitated and the powders are formed through nucleation and growth. This method is suitable, simple, and effective controlled synthetic process and cheap because water is solvent [25].

Li et al. [26] used the low temperature hydrothermal method to synthesize nanosized $Y_2Sn_2O_7$ composite with the particle size from 10 to 300 nm using different organic agents. They demonstrated that these nanocomposites can be shown photocatalytic properties in water purification.

3.3 Combustion

When metal precursors (oxidants) and fuel react using combustion, these reactions can cause to produce rare-earth-based powders. In this method, a mixed solution consists of rare-earth material as precursors and urea as fuel were prepared then other solution (pH control agent) was added to this solution for gel formation. The prepared gel was dried and heated at high temperature to obtain rare-earth-based nanostructures [7, 27].

Zinatloo et al. [13] used combustion method to fabricate $Nd_2Sn_2O_7$-SnO_2 nanocomposites as novel and non-toxic biofuel using extract of pineapple. They showed that produced nanocomposites had high photocatalytic activity to degrade environmental pollution.

3.4 Coprecipitation

In the coprecipitation technique, the hydroxides are instantaneously precipitated from precursor solutions via adding a base solution. The formed hydroxide precipitates is then calcined to prepare rare-earth nanostructures. Ziarati et al. [28] synthesized $NiFe_{2-x}Eu_xO_4$ nanostructure using coprecipitation method and calcination. They showed that samples had high yields in presence of the rare-earth-based catalyst.

3.5 Sol-gel

In the sol-gel technique, hydrolysis and poly-condensation reactions of metal alkoxides occur to form gels. Afterwards, the achieved gels are calcined to obtain rare-earth nanoparticles. The sol-gel technique is low-cost, simple, friendly to the environment and less complicated than the others [7].

Li et al. [2] synthesized $LnFeO_3$ (Ln = Pr, Y) powders using sol-gel method with utilizing, lanthanide metal (Ln = Pr, Y) with the assistance of glycol at 800°C for 4 h. Photodecomposition rate of RhB was improved by $LnFeO_3$(Ln = Pr, Y) nanoparticles.

Nowadays, there are different ways for the production of rare-earth nanostructure such as sol-gel combined electrospinning, complex precipitation, pechini polymeric route, molten salt synthesis, co-ions complexation method, Cathode plasma electrolysis, Complex precipitation method, Precursor route and Floating zone technique.

3.6 Advantages and disadvantages of these methods

In this section, the advantages and disadvantages of each preparation technique have been discussed, briefly. Some nanostructured samples in this chapter have been synthesized using various methods by our research group.

There are different wet chemistry techniques to synthesize rare-earth-based nanostructures with suitable properties. In the wet chemistry technique, materials are mixed with together therefore the final powders have excellent compositional homogeneity. However, the solid state reaction technique is one of them that can cause the undesirable properties of final powders such as poor control of morphology and particle size and nonhomogeneity of distribution [23].

Hydrothermal method is homogeneous nucleation processes as remarkable advantage that can cause to synthesize particles with small size without the calcination stage. However, reaction rate and formation of rare-earth nanostructures are slow thus, a moderate heating stage at low temperature is necessary after the hydrothermal stage to accelerate the solid reaction [25].

The combustion technique can cause to synthesize powders with high purity, small size and uniform distribution. Nevertheless, the combustion reaction is not easy to control. Also, the combustion reaction can lead to agglomeration of the formed nanoparticles due to high temperature [27].

Coprecipitation method can lead to synthesize high purity compounds with a homogeneous composition at relatively low temperature but the obtained powders have large size. Thus a grinding stage is essential to synthesize a compound with small size [29, 30].

The sol-gel method is as an appropriate technique for compositional controlling the metallic species that the final powders are prepared through calcining stage with small size [31].

The type of method is effective on the characteristics of the powder therefore, selection of the right method is essential to prepare the powder with small particles, high uniform and purity. Also energy and cost is important to choose method.

4. Application of rare-earth-based material

Rare-earth-based materials were used in different fields. Some of rare-earth materials have been used for multipurpose applications such as gas sensors, solar cells, rechargeable batteries, supercapacitors, and transparent conducting electrodes, electronic and optical properties. The rare earth doped with some semiconductors such as SnO_2 can be used for temperature sensing. Recently, Eu^{3+}-ions doped SnO_2 has attracted the research attention as a candidate for thermometry applications [5].

Also, rare-earth-based perovskite oxides can be applied as catalysts for low-temperature fuel cells. The dimensions of the unit cell can be changed by varying the lanthanide ion which this unique property is an interesting characteristic of rare-earth perovskites ($LnMO_3$) [2].

According to the information of other researchers, rare-earth-based perovskites have been applied as fuel cell catalysts for methanol oxidation and oxygen reduction in alkaline medium. The results showed that these materials enhanced the kinetics of the methanol oxidation reaction in alkaline medium. On the other hand rare-earth-based perovskite oxides were used as cathode and anode catalysts for oxygen reduction in alkaline medium [9].

Rare-earth-based materials such as CeO_2 also were added as an additive for Nafion membranes to improve their chemical stability. Hydrogen peroxide and its decomposition produce $HO^{\cdot}$ and $HOO^{\cdot}$ during the fuel cell operation that they have been considered as a key factors leading to membrane degradation therefore, CeO_2 nanoparticles act as mitigating free-radical-induced or free radical scavenger in biological systems due to their higher surface area and ability to undergo faster redox reaction. All studies suggested that CeO_2 nanoparticles have incredible potential to improve membrane permanence [4].

In this section, we study a brief review of rare-earth-doped materials, rare-earth-based oxide-oxide composites, metal-modified semiconductors and mixed-oxide materials in the fields of photocatalytic application as solar energy generation (**Figure 1**) [9].

Rare-earth-based material play a key role in important photocatalytic and energy production processes such as catalysts. Rare-earth material such as the lanthanide elements can perform as catalysts to enhance the efficiency by:

1. Developing properties of the catalyst surface,

2. Improving the thermal stability of catalytic oxides,

3. Enhancing the catalytic efficiency due to their redox capabilities and conductivity development,

4. Increasing oxygen uptake [9].

After a brief introduction of rare-earth materials and their properties ions and oxide materials. In the next sections will be discussed perspectives of rare-earth materials in photocatalytic processes and their potential as active catalysts or support materials.

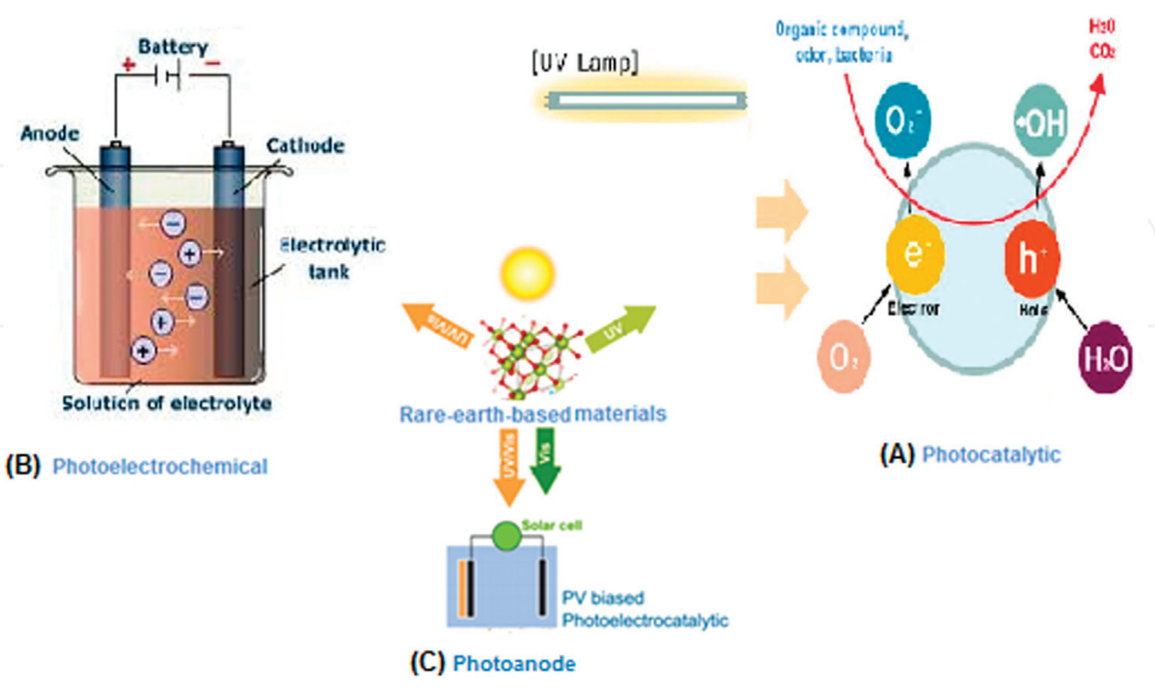

Figure 1.
Applications of rare-earth-based materials in solar energy generation: (A) photocatalytic, (B) photoelectrochemical, (C) cell approach (photoelectrocatalytic).

4.1 Heterogeneous photocatalysis

One of the progressive knowledge is heterogeneous photocatalysis that can be applied in diverse fields. Photocatalytic materials are used to degrade organic and inorganic pollutants in both the vapor and liquid phases [6].

When a photon is absorbed by rare-earth-based material using the energy gap of the materials, electron-hole pairs are generated in the photocatalysis mechanism.

Photocatalyst	Synthetic method	Light source	Removal percentage (%)	Ref.
RVO_4; R 5 La, Ce, Nd, Sm, Eu and Gd	Sonication	8 W mercury UV lamps of 365 nm wavelength	70% of methylene blue after 90 min illumination	[1]
$LnFeO_3$ (Ln = Pr, Y)	Sol-gel	500 W Xe lamp	96% of RhB after 2 h illumination	[2]
La-doped TiO_2	Sol-gel	UV irradiation at specific wavelength, 254 or 365 nm	≥90% of methylene blue after 90 min illumination	[8]
$Dy_2Ce_2O_7$	Green synthesis using juice of Punica	125 W Osram lamp	92.8% of methylene blue after 70 min illumination	[10]
$Dy_2Sn_2O_7$-SnO_2	Pechini	400 W mercury lamps	81% of methyl orange after 50 min illumination	[11]
$Nd_2Sn_2O_7$	Green synthesis using pomegranate juice	125 W Osram lamp	96.7% of methyl violet after 70 min illumination	[12]
$Nd_2Sn_2O_7$-SnO_2	Combustion	125 W Osram lamp	88.7% of rhodamine B after 70 min illumination	[13]
Nd_2O_3	Simple precipitation	125 W mercury lamps	89.6% of methylene blue after 90 min illumination	[14]
Ho_2O_3-SiO_2	Sonochemical	125 W mercury lamp	94.9% of methylene blue after 70 min illumination	[15]
Ho_2O_3	Sonochemical	125 W mercury lamp	82.2% of erythrosine after 70 min illumination	[16]
Nd_2O_3-SiO_2	Sonochemical	125 W Osram lamp	93.1% of methyl violet after 70 min illumination	[17]
$Nd_2Zr_2O_7$–ZrO_2	Modified Pechini	400 W mercury lamps	85% of methylene blue after 50 min illumination	[20]
$Pr_2Ce_2O_7$	Pechini	400 W mercury lamps	92.1% of methyl orange after 50 min illumination	[35]
$GdFeO_3$	Sol-gel	500 W Xe lamp	100% of RhB after 2 h illumination	[36]
$Dy_2Ce_2O_7$	Green synthesis using *Ananas comosus*	125 W Osram lamp	91.7% of black T after 1 h. illumination	[37]
$Dy_2Ce_2O_7$	Green synthesis using *Vitis vinifera* juice	125 W Osram lamp	92.4% of methyl orange after 80 min illumination	[38]
Nd_2O_3	Hydrothermal	UV light from the 400 W mercury lamps	79% of black T after 100 min illumination	[39]

Table 1.
Rare-earth-based materials for photocatalytic application in the degradation of organic pollutants.

Therefore light absorption with energy equal to or greater than the band gap of the material can cause an electron to be excited from the valence band to the conduction band [32]. These electrons and holes can be recombination with together that it is a major limiting factor to control its photocatalytic efficiency in the degradation of pollutant. Therefore, selection of material is a major challenge in heterogeneous photocatalysis that rare-earth-based nanostructure can be increased the efficiency of the photocatalysts [33]. To improve the efficiency of photocatalysis and reduce the recombination of electrons and holes, modification of rare-earth-based material is necessary. Therefore these materials have been doped with various transition metal ions [34]. The photocatalytic mechanism to degrade the pollutant contaminant may write as below [35]:

Prepared nanostructures + $h\upsilon \rightarrow$ Prepared nanostructures ($e^{-}_{(CB)} + h^{+}_{(VB)}$).
$OH^{-} + h^{+}_{(VB)} \rightarrow OH^{\cdot}$
$O_2 + e^{-}_{(CB)} \rightarrow O_2^{\cdot -}$
$O_2^{\cdot -} + H^{+} \rightarrow HO_2^{\cdot}$
$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow O_2 + H_2O_2$
$H_2O_2 + O_2^{\cdot -} \rightarrow OH^{\cdot -} + OH^{\cdot} + O_2$
$OH^{\cdot}$ + Organic $\rightarrow$ Intermediates $\rightarrow CO_2 + H_2O$ + Products

4.2 Photocatalytic applications

Rare-earth-based materials are applied as catalysts in different industrial applications, e.g., petroleum refining (lanthanum chloride), automobile emission reduction (cerium oxide), organic polymerization (neodymium versatate), hydrogen and synthesis gas production (ceria, lanthania), plastics decomposition, and dechlorination (samarium iodide), solar thermochemical water splitting and photocatalytic reactions have been investigated thoroughly, especially for La^{-}, Ce^{-}, Eu^{-}, and Gd^{-} modified materials [9].

The mixed oxide photocatalysts have attracted attention because of their abilities to remove pollutant or split water into H_2 and O_2 under solar irradiation. Among the mixed oxides, rare-earth-based materials contained mixed oxide photocatalysts are important, because the 4f-levels of lanthanide elements play a key role in photocatalytic reactions. Some researches are shown in **Table 1** that they include photocatalysts of rare-earth elements for degradation of organic pollutants. For example, Zinatloo et al. [13] synthesized $Nd_2Sn_2O_7$-SnO_2 nanocomposites as high-efficiency visible-light responsive photocatalyst through an environment-friendly procedure (Green synthesis) using extract of pineapple. Extract of pineapple that employed in this research, is natural source of sugar (glucose as well as fructose) and harmless for the environment.

5. Conclusions

This book chapter includes the recent advances related to synthesis method and photocatalytic applications of rare-earth-based nanostructures. Several techniques for preparation of rare-earth-based nanostructures have been introduced to achieve nanostructure with desirable characterizes.

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