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Synthesis and Application of New Nanomaterials Doped with Lanthanide Elements

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By

Rana Helmy Abdo Abd Elhamid Gabr

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(Inorganic Chemistry)

To

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Ain Shams University
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A novel Dy^{3+} modified $Zn_2Ti_3O_8$ nanoparticles for efficient hydrogen production photocatalysis

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ABSTRACT

Novel Dy^{3+}:$Zn_2Ti_3O_8$ (Dy^{3+}:ZTO) nano-photocatalysts with different Dy^{3+} concentrations were applied to enhance the photocatalytic hydrogen generation activity from sodium borohydride hydrolysis reaction. XRD and Raman measurements confirm the formation of cubic $Zn_2Ti_3O_8$ phase as a major phase in addition to minor TiO_2 phase. The analysis of XPS spectra shows the existence of lattice oxygen (LO) and non-lattice oxygen (NLO) where 0.07 mol Dy^{3+}:ZTO has the highest percentage of NLO compared to the undoped photocatalyst. The energy gap value decreases with increasing doping concentrations (3.137 eV for 0.07 mol Dy^{3+}:ZTO). The degree of disorder, represented by Urbach energy, has an optimum high value (0.169 eV) for 0.07 mol Dy^{3+}:ZTO. The photoluminescence studies revealed that Dy^{3+} dopant can effectively separate the photogenerated electron/hole pairs in the ZTO. These photocatalysts have strong photocatalytic hydrogen generation. The most active nano-photocatalyst towards hydrogen generation was 0.07 mol Dy^{3+}: ZTO (5.6 mmol/g). The highest photocatalytic activity for 0.07 mol Dy^{3+}: ZTO are attributed to the lower recombination rate associated with the higher disorder and oxygen vacancies relative to the undoped photocatalyst. The stability and reusability of the most active photocatalyst were investigated. The results confirm that the developed photocatalyst has good durability in hydrogen generation reaction. The results, moreover, revealed that Dy^{3+}: ZTO nano-photocatalyst is a promising nanomaterial in the field of energy production.

1. Introduction

Energy can be counted as one of the basic requirements of human life. Economic and industrial development strongly depends on fossil fuels such as coal, oil, and natural gas with almost 80% [1]. Although carbon-based energy sources have made an industrial revolution, they still have a negative impact on the environment. This is attributed to the release of different greenhouse gases, global warming and huge amount of wastes [2–4]. The high price of fossil fuels, depletion of natural resources as well as environmental concerns have forced scientists to search for clean and renewable energy alternatives including solar, wind, and hydrogen energy [5,6]. One of the most promising alternatives for fossil fuels seems to be hydrogen energy [7]. Hydrogen is widely considered as an environmentally-friendly, economic and energy-efficient fuel. It plays an important role in the elimination of CO_2 [8]. The calorific value of hydrogen (140.4 MJ/kg) is 3–4 times that of fossil fuels such as coke and gasoline [8]. Various methods have been applied to hydrogen production such as electrolysis, fossil energy steam reforming, biomass pyrolysis, thermochemical hydrolysis of hydrides, electrochemical and photocatalytic water splitting, etc. [9,10].

The hydrolysis of borohydrides is an interesting technique to produce pure hydrogen energy. Sodium borohydride compound is an ideal source of hydrogen through the interaction with water due to its high gravimetric hydrogen content (10.8 wt%), low cost, great stability and liberation of hydrogen in safe and controllable manner. This process can be carried out according the following equation [11,12]:

$$NaBH_4 + 4H_2O \rightarrow NaB(OH)_4 + 4H_2 \quad (\Delta H^0 = -210 \quad kJ/mol).$$

The acceleration of borohydride hydrolysis rate using acids, transition metal salts and catalysts were reported by different

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research groups [9,13,14]. However, this method is still limited as an energy source for different applications. This is attributed to the small amount of hydrogen produced by this method [9].

Photocatalytic water splitting is an emerging technology that has been recently used for hydrogen production [15,16]. This method has several advantages including cost-efficiency, facilities, and suitability for residential applications [17]. In this method, the photocatalysts are illuminated with solar energy (UV and/or visible) to form electrons and holes in the conduction and valence bands, respectively. The produced charge carriers split water molecules into oxygen gas and hydrogen ions according to the following overall decomposition reaction $2\,h\upsilon + H_2O$ (liquid) $\rightarrow 1/2\,O_2$ (gas) $+ H_2$ [17,18]. Several systems are investigated for photocatalytic water splitting such as bimetallic combined with reduced graphene [18], carbon based nanomaterials [19], $MTiO_3$ [20], TiO_2–$ZnIn_2S_4$ [21], $ZnIn_2S_4$ @PCN-224 [22]. Li et al. [23] used NiFe-metal-organic frameworks (NiFe-MOFs) as a cocatalyst with $BiVO_4$ photoanode for water splitting. However, this method is still limited by rapid electron/hole recombination. But this limitation can be treated by different strategies such as doping, composite, preparation methods, using capping agent… etc. [23,24]. Zhang et al. [25] Proved that amino-functionalized titanium dioxide can accelerate the photocatalytic water splitting rate. Li et al. [26] improves the photocatalytic hydrogen generation activity of TiO_2 by Pt nanoparticles. Song et al. [27] reported that Cu_7S_4/$MnIn_2S_4$ composite improves the photocatalytic hydrogen evolution activity from water.

In view of this, it seems to be beneficial to improve the hydrogen production efficiency via adopting the hydrolysis of borohydrides in presence of highly efficient photocatalytic systems. Literature data concerning photocatalytic generation of hydrogen from borohydride hydrolysis reaction are very limited. Lee et al. [28] investigated hydrogen production from the photocatalytic hydrolysis of sodium borohydride in presence of In–, Sn–, and Sb–TiO_2. Lin et al. [29] studied the photocatalytic hydrolysis of alkali-metal in presence of P25 for hydrogen generation. Unfortunately, no significant progress in this area has been accomplished since then.

ZnO-TiO_2 composite system has several advantages such as high separation rate of photogenerated carriers, wide band gap energy and wide optical response range. ZnO-TiO_2 composite contains three crystal phases: zinc metatitanate $ZnTiO_3$, zinc orthotitanate Zn_2TiO_4 and zinc polytitanate $Zn_2Ti_3O_8$ [30]. $Zn_2Ti_3O_8$ phase can produce hydrogen at low annealing temperature compared to other phases. $Zn_2Ti_3O_8$ phase have been synthesized and studied from a structural and electrical point of view [31,32]. It was also used in lithium-ion batteries [33]. However, no attempts of using $Zn_2Ti_3O_8$ and its lanthanide doped (Dy^{3+} doped $Zn_2Ti_3O_8$) in a photocatalytic generation of useful hydrogen energy from hydrolysis of sodium borohydride can be found among literature data. It was reported that doping of the photocatalysts with lanthanide ions reduces the (e-/h+) recombination effectively. Moreover, lanthanide doping acts as complexation centers on the photocatalyst surface, thus enhancing its activity [24,34–36].

Considering the above stated data, we have focused in the present study on the preparation of novel photocatalyst based on Dy^{3+} doped $Zn_2Ti_3O_8$ and its application for the generation of useful hydrogen energy.

2. Experimental

2.1. Materials and methods

All chemicals were of analytical grade. Dy_2O_3, $Zn(NO_3)_2x6H_2O$ and Titanium isopropoxide $Ti(OC_4H_9)_4$, Sodium borohydride (NB), nitric acid, ethanol, and glacial acetic acid; all were purchased from Sigma- Aldrich. $Dy(NO_3)_3$ was prepared by reaction of dysprosium oxide (Aldrich) and nitric acid.

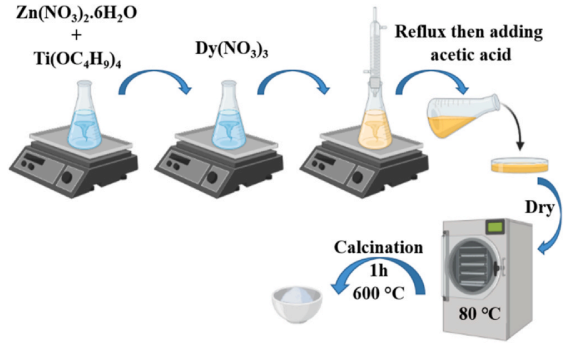

Fig. 1. Schematic illustration for Dy^{3+}: ZTO prepared by sol-gel method with different Dy^{3+} concentrations.

2.2. Synthesis of Dy^{3+}: $Zn_2Ti_3O_8$ nano-photocatalysts

Nano-photocatalysts based on x mol Dy^{3+}:$Zn_2Ti_3O_8$ (x mol Dy^{3+}:ZTO; x = 0.01, 0.03, 0.05, 0.07 and 0.09 mol) were synthesized via sol-gel technique. Initially, certain amounts of $Zn(NO_3)_2.6H_2O$ and $Ti(OC_4H_9)_4$ with stoichiometry (Zn/ Ti = 2:3) were dissolved into ethanol (25 ml), Then 0.00, 0.01, 0.03, 0.05, 0.07 and 0.09 mol of Dy^{3+} salt were added to the above mixture as dopant under continuous stirring. The mixture was, then, refluxed at ethanol boiling point for 3 h under continuous stirring. Concentrated acetic acid (100%) was added drop by drop to the above mixture to adjust the pH value to 1–2. Transparent sol of pale-yellow color was obtained. The sol was, then, heated to 80 °C slowly and dried. Finally, a brown puffy gel was obtained. The dried gel was calcined at 600 °C for 1 h and the obtained powders were used for further analysis (Fig. 1).

2.3. Characterization

The prepared samples were characterized with transmission electron microscopy (TEM, JEM-2100(JEOL)), operating at 200 kV accelerating voltage. The X-ray diffraction (XRD) patterns were recorded by 'PHILIPS' diffractometer with CuKα1 radiation (kα = 1.54056 Å). An accelerating voltage of 40 kV and an emission current of 30 mA were applied. The UV–Vis. diffuse reflectance (DR) spectra of the prepared samples were recorded using 'JASCO V-530′ spectrometer (Japan), equipped with an integrating sphere accessory to diffuse reflectance spectra. $BaSO_4$ was used as a reference. The photoluminescence emission was measured using a 'Perkin Elmer LS55′ Luminescence Spectrometer (USA). Raman spectra were obtained from Senterra equipment using a wavelength of λ = 532 nm as excitation. Analysis of the surface components of the samples was carried out by applying X-ray photoelectron spectroscopy (XPS, AXIS Nova) with Al Kα monochromatized radiation. The peak position was calibrated by using the binding energy position of C1s, which is more common, so it is taken as a reference. Brunauer–Emmett–Teller (BET) surface area and pore size distribution (PSD) of the samples were evaluated by operating an N_2 adsorption-desorption apparatus (3FlexSurface Characterization Analyzer, Micromeritics Instrument Corp.) at a temperature of −196 °C. Before performing the adsorption–desorption experiments, all samples were degassed at 180 °C for 12 h. The BET-specific surface area was calculated by applying BET equation and PSD was obtained via Barrett–Joyner–Halenda (BJH) method.

2.4. Hydrogen production from catalytic hydrolysis of sodium borohydride solution using Dy^{3+}: $Zn_2Ti_3O_8$ photocatalysts

For hydrogen generation, the hydrolysis was performed in standard water-filled gas using an inverted volumetric cylinder system to