



Visible light responsive TiO₂ nanoparticles modified using Ce and La for photocatalytic reduction of CO₂: Effect of Ce dopant content

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ABSTRACT

Photocatalytic reduction of CO₂ in aqueous solution was performed using TiO₂ photocatalysts modified with Ce and La under fluorescent light irradiation. The photocatalysts were prepared using modified sol–gel method with Ce doping content varied between 0 and 2 wt%. Comprehensive characterization using XRD, XPS, nitrogen physisorption, SEM, EDX, PL and UV–vis spectroscopy revealed that the introduction of cerium affected the surface, structural and optical properties of the photocatalysts. Among all the doped photocatalysts, 1.5 wt% Ce/La/TiO₂ showed the highest photocatalytic activity under fluorescent light irradiation. In the liquid phase, a maximum yield of 317.7 μmol/g cat for CH₃OH was achieved whereas CH₄ and CO were the main products in the gas phase with maximum yields of 262.8 and 119.4 μmol/g cat, respectively. The addition of Ce and La was found to inhibit the growth of anatase TiO₂, increase the surface area and improve the optical properties of the photocatalyst. The existence of Ce³⁺/Ce⁴⁺ mixture was also found to effectively inhibit the electron–hole recombination, enhancing the photocatalytic activity of Ce/La co-doped TiO₂.

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1. Introduction

Global warming and its effects on the environment, human society and the planet in general have been the center of attention for the past decade. Burning of fossil fuels such as coal and oil in industries and also transportation will result in strong liberation of greenhouse gasses and their accumulation in the atmosphere [1,2]. Carbon dioxide (CO₂) among other greenhouse gasses has been blamed as one of the causes of global warming. A prospective way to reduce CO₂ emission and at the same time produce renewable source of energy is through photocatalytic reduction of CO₂ with H₂O [3,4]. According to the band gap model, rate of photocatalytic reaction depends on the type of photocatalyst and also the source of irradiation used [5,6]. To date, a number of catalysts have been investigated such as ZnS, CdS, ZrO₂, MgO, and ZnO [7–9]. Among these catalysts, TiO₂ has been widely used due to its low cost, low toxicity, high photostability and strong reduction properties [63]. Having said that, TiO₂ has fairly wide band gap (~3.0 eV for rutile and ~3.2 eV for anatase) which makes it only responsive to UV light [10].

In order to improve TiO₂ photocatalytic efficiency, TiO₂ has been doped with various transition metals, noble metals and nonmetals. It was found that doping of TiO₂ with transition metals enhanced visible light absorption but the photocatalytic performance under UV light decreased significantly [11,12]. As for nonmetal dopants, the photocatalytic activity was generally improved, but at the expense of the thermal stability of the photocatalyst [13]. Noble metal introduction was found to reduce electron–hole re-combination, but it did little in extending the light absorption into the visible region [12]. Thus, it is important to seek other dopants that can overcome these disadvantages. Doping of TiO₂ with rare earth metals, lanthanide ions in particular, could be an interesting approach [14]. The incompletely occupied 4f and 5d orbitals of the lanthanide ions provide high electrical conductivity and thermal stability to their oxides [15,16]. Furthermore, lanthanide ions can also reduce electron–hole recombination rate by trapping the excited electrons [17].

In recent years, the incorporation of lanthanides ions such as lanthanum (La) and cerium (Ce) has been reported to improve the photocatalytic activity of TiO₂ photocatalysts [18,19]. Anandan et al. [20] found La doped TiO₂ photocatalyst to be very active and its rate constant was 2.33 and 1.75 times higher than that of TiO₂ and La doped ZnO, respectively. Cong et al. [21] reported that the 4f electron configuration of La ions not only could improve the photocatalytic activity of the photocatalyst, but it could also inhibit

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anatase to rutile transformation at higher temperature. As for Ce, Zhao et al. [22] found that Ce doping improved the production of CO by four times due to the presence of Ce that could facilitate the charge transfers. The study conducted by Matějová et al. [18] indicated that the performance of Ce doped TiO₂ in the photocatalytic reduction of CO₂ was attributed by the energies of electrons and holes within the electronic structure of the photocatalyst, which was governed by the amount of Ce added.

Therefore it would be interesting to study the effect of simultaneous addition of both Ce and La on the photocatalytic reduction of CO₂. Thus far, most of the reported works on the photocatalytic processes for photoreduction CO₂ in the literature have been limited to mono doped TiO₂ photocatalyst. Addition of two metals into TiO₂ photocatalyst could efficiently compensate the limitation of mono doping. It has been reported that the introduction of a second rare earth metal could serve as a bridge between TiO₂ and the first dopant to increase the energy transfer efficiency which might be low due to the mismatch in energy between TiO₂ and the first dopant [23]. The production of CO from the photocatalytic reduction of CO₂ using nickel and indium co-doped TiO₂ as reported by Tahir and Amin [24] was 1.6 and 6.3 times higher than that of Ni and In doped TiO₂, respectively.

In the quest for the enhancing the photocatalytic reduction of CO₂ process efficiency, a series of Ce and La co-doped TiO₂ photocatalysts along with La doped TiO₂ were prepared using a simple sol-gel method. The photocatalytic test was conducted in slurry reactor under fluorescent light irradiation. To the best of our knowledge, this is the first time Ce and La co-doped photocatalyst is used for CO₂ photoreduction under fluorescent light irradiation using a simple slurry reactor. In the present work, the effects of type and amount of dopant on the structural, optical and surface properties as well as on the photocatalytic activity for photocatalytic reduction of CO₂ was demonstrated. The stability and reusability test of Ce and La co-doped TiO₂ in a slurry reactor were also investigated.

2. Experimental

2.1. Chemicals

Absolute ethanol and glacial acetic acid were purchased from Merck. Tetrabutyl orthotitanate (Ti(O(C₄H₉))₄) was purchased from Acros Organics and cerium (III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O) and lanthanum (III) nitrate hexahydrate (La(NO₃)₃·6H₂O) were purchased from Fluka. Deionized and distilled water was used for hydrolysis and washing, respectively. All the chemicals were used as received without any purification.

2.2. Catalyst preparation

Pure TiO₂, La doped TiO₂ and a series of Ce and La co-doped TiO₂ photocatalysts (with 0.5, 1, 1.5 and 2 wt% of Ce) were synthesized using a modified sol-gel method [25]. The amount of La used for La doped TiO₂ and Ce and La co-doped TiO₂ was not varied and fixed at 2 wt%. The synthesis method for pure TiO₂ was as follows: 5 ml of glacial acetic acid and 10 ml of absolute ethanol were added into 10 ml of tetrabutyl titanate under continuous stirring condition (solution A). 4 ml of deionized water, 6 ml of acetic acid and 30 ml of ethanol were mixed together to form solution B. Solution A was then added dropwise into solution B with constant stirring for 30 min. The solution was then sealed and heated up to 60 °C for 2 h under continuous stirring. The resultant gel was then aged at 0 °C for 24 h and dried in an oven at 80 °C. The samples were washed with distilled water to remove any un-reactant chemical and dried again at 80 °C. The dried samples were then milled using an agate mortar followed by calcination at 500 °C for 4 h at a heating rate of

1 °C/min. In the case of mono- and co-doped TiO₂ photocatalysts, appropriate amounts of Ce and La salt were added into deionized water.

2.3. Characterization

The crystal structure of the synthesized photocatalysts were identified using X-ray diffractometer (Siemens 2000x series) with Cu- α radiation ($\lambda = 1.5406 \text{ \AA}$), operated in the range of $2\theta = 20\text{--}90$. The crystallite size of the photocatalysts was calculated by using the Scherrer's equation, $D = K\lambda/\beta\cos\theta$ where D is the average crystallite size (nm), K is the Scherrer constant (0.89), λ is the wavelength of the X-ray source, β is the full width at half maximum and θ is the Bragg's angle. The crystallite size of the photocatalysts was calculated with respect to anatase (101) plane. Nitrogen sorption isotherms were obtained using a Micromeritics ASAP 2020 surface analyzer. Based on the nitrogen adsorption/desorption isotherms, surface characteristic including BET surface area, total pore volume and average pore size were calculated. Scanning electron microscope (SEM) analysis was performed using a Quanta 450 FEG scanning electron microscope equipment operated at 15 kV. The elemental composition on the surface of the photocatalyst was determined using Oxford X-max energy dispersive X-ray (EDX) system using Mn K α as the energy source that was attached to the SEM unit. Photoluminescence (PL) spectroscopy was carried out using a Perkin Elmer Lambda S55 spectrofluorometer using a Xe lamp with an excitation wavelength of 290 nm. The X-ray photoelectron spectroscopy (XPS) was conducted using Kratos Axis Ultra DLD High Resolution Multi Technique X-ray spectrometer. The XPS spectrum was recorded using an analyzer with the pass energy of 40 eV and X-ray power of 225 W. The XPS data was analyzed using CasaXPS software to obtain information regarding the state and composition of the species present on the surface of the photocatalysts. The diffuse reflectance spectra of the photocatalysts were recorded using Perkin Elmer Lambda 35 UV-vis spectrophotometer and BaSO₄ was used for baseline correction. The obtained reflectance data was converted to equivalent absorption spectra and was used to estimate band gap energy of the photocatalysts using Kubelka-Munk function (Eq. (1)).

$$F(R) = \frac{(1 - R)^2}{2R} \quad (1)$$

2.4. CO₂ photoreduction test

The photoreduction of CO₂ with H₂O was carried out in a stirred batch annular reactor with a volume of 500 ml with suspended catalyst. A 15 W fluorescent lamp (Osram DULUXSTAR MINI TWIST 11W/826 E27) was used as the light source for visible light irradiation. The lamp was situated at the center of a quartz tube. NaOH 0.2 M was used as the reaction medium with a catalyst loading of 1 g/L. Supercritical fluid-grade CO₂ with a certified maximum hydrocarbon less than 1 ppm was used as the carbon source. Prior to the illumination, N₂ gas was bubbled at a constant rate for 30 min to make the reaction environment inert. Then, CO₂ gas was bubbled in at a constant rate (20 cm³/min) to purge the N₂ and saturate the solution. Liquid and gaseous samples were taken every 30 min for product analysis using gas chromatograph (GC). For gaseous sample, a GC equipped with thermal conductivity detector (TCD) and a carbon molecular sieve (carbolite) column with H₂ as carrier gas was used. Certified calibration gases were used to calibrate the GC before each experimental run. The gases were injected into the GC to determine the retention time and peak areas for each component. The liquid sample was analyzed using a GC equipped with thermal conductivity detector (TCD) and a molecular sieve (Hysep-T) column for hydrocarbon analysis with He as the carrier gas. All

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