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Hydrogen production from water–methanol solution over visible light active indium–titanium oxide photocatalysts modified with copper oxide

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ABSTRACT

Titanium oxide coupled with different amount of indium oxides were studied for production of hydrogen under visible light irradiation from water–methanol solution. The photocatalysts were prepared by co-precipitation and characterized by surface area and pore analysis, X-ray diffraction, field emission scanning electron microscopy, UV–Vis diffuse reflectance spectra, and photoluminescence spectroscopy. With increases in indium oxide content, the surface area, visible light absorption and separation of photo-generated electron–holes were enhanced. For binary catalysts, the activity was highest for 16.7 at.% indium with hydrogen production of 1829 $\mu\text{mol/g/h}$. Incorporation of copper oxide further enhanced the activity with hydrogen production of 2149 $\mu\text{mol/g/h}$. The higher hydrogen production for ternary catalyst can be attributed to the synergistic effects of higher surface area, stronger absorption in visible light region and enhanced separation of photogenerated charge carriers. The hydrogen generation was attributed to partial oxidation of methanol to formaldehyde thereby producing pure hydrogen.

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Introduction

The generation of hydrogen using renewable sources is an attractive way to simultaneously meet the increasing demand of energy as well as minimizing the environmental pollutions. Hydrogen has received greater attention as an ideal energy carrier for the future due to its higher energy content compared to that of other fuels [1]. Photocatalysis is one of the most promising ways to produce hydrogen by utilizing the renewable sources such as solar energy. In the past decade, several strategies have been developed to increase the photoactivity of TiO_2 for hydrogen production from water or

water–alcohol mixtures, such as noble metal loading, doping with metallic or non-metallic elements and dye sensitization [2]. Another effective way to improve the photocatalytic efficiency is to form heterostructures by coupling TiO_2 with other narrow band gap semiconductors and extend the optical absorption of wide band gap semiconductor to higher wavelength [3].

Wang et al. [4] studied the ZnO/CdS heterostructures with enhanced photocatalytic activity for hydrogen production and attributed improved hydrogen evolution to the prolonged lifetime of the charge carriers of the coupled heterostructures. Ma et al. [5] attributed enhanced photocatalytic activity of $\text{MoO}_3/\text{TiO}_2$ catalyst for hydrogen production from methanol

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solution to the separation of electron–hole pairs and two half reactions of the photocatalysts into two semiconductors. Jang et al. [6] reported high hydrogen production on CdS/TiO₂ composites compared to their single oxides. Many studies have been reported on binary composites for hydrogen production under visible light irradiation, but the investigation of ternary systems is still limited. The photocatalytic efficiency is reported to improve further for ternary system due to the decrease in electron–hole pair recombination. Zhang et al. [7] reported the photocatalytic hydrogen production over Cr₂O₃–SiC–TiO₂ under visible light irradiation while, Park et al. [8] prepared a ternary system of CdS/TiO₂/Pt for hydrogen production under visible light irradiation. Recently Liu et al. [9] reported higher photocatalytic activity for In₂S₃–Pt–Na₂Ti₃O₇ compared to that of In₂S₃–Na₂Ti₃O₇ catalyst under visible light irradiation.

In the present work, titanium oxide was coupled with indium oxide and studied for photocatalytic hydrogen production from water–methanol system under visible light irradiation. In₂O₃ is an important n-type semiconductor material with a direct bandgap of 3.6 eV and an indirect bandgap of 2.8 eV [10]. Further, a ternary system of copper, indium and titanium oxides was prepared and investigated for photocatalytic hydrogen production. The aim of this work was to develop visible light active photocatalysts for hydrogen generation from water–methanol system. This will enhance the use of renewable sources as well as provide a route for utilization of CO₂ pollutant through methanol. The properties of the photocatalysts were determined using various characterization techniques and correlated with their photocatalytic activity.

Materials and methods

Materials used

Titanium tetra isopropoxide (C₁₂H₂₈O₄Ti, 97%) was procured from Sigma–Aldrich and Indium nitrate (In(NO₃)₃, 99.99%) was obtained from Alfa Aesar. Copper nitrate trihydrate (Cu(NO₃)₂·3H₂O, ≥99%), isopropanol (C₃H₈O, ≥99%), sodium hydroxide pellets (NaOH, 98%), D-glucose (C₆H₁₂O₆·H₂O, >99%) and methanol (CH₃OH, 99.8%) were purchased from Merck.

Preparation of photocatalyst

The coupled indium–titanium oxide system was prepared by co-precipitation. The required amount of titanium tetra isopropoxide was dissolved in isopropanol under stirring condition for about 30 min. Required amount of indium nitrate was dissolved in deionized water and the solution was added drop wise to the titanium tetra isopropoxide solution. The resultant mixture was stirred continuously for another 30 min. Thereafter, sodium hydroxide solution (0.3 mol/l) was added to the above mixture with continuous stirring until precipitation was complete. The obtained solution was transferred to a round bottom flask attached to a reflux condenser and was aged at 353 K for 5 h. After washing and filtration, the precipitate was dried at 373 K overnight and calcined at 823 K for 4 h to obtain indium–titanium binary oxide samples with

different indium content. The prepared samples are designated as 5%In–Ti, 10%In–Ti and 16%In–Ti containing 4.3, 9.5 and 16.7 at.% indium as determined by energy dispersive spectroscopy (EDS). For comparison pure titanium oxide and pure indium oxide were also prepared by similar precipitation procedure.

The copper doped indium–titanium ternary oxide system was also prepared by co-precipitation. The solution containing titanium tetra isopropoxide and indium nitrate was prepared as described above. Thereafter, aqueous solution containing required amount of copper nitrate and D-glucose (0.1 mol/l) was added drop wise to the above solution of isopropoxide and indium nitrate. The precipitation was carried out by adding sodium hydroxide solution (0.3 mol/l) slowly to the resultant mixture under stirring until the precipitation was complete. The mixture was refluxed for 5 h at 353 K. After washing and filtration, the precipitate was dried at 373 K overnight. The dried sample was calcined at 823 K for 4 h to obtain the ternary oxide. In copper doped indium–titanium ternary oxide, the contents of In and Cu were 8.6 and 1.9 at.% respectively as determined by EDS. The sample was designated as 2%Cu–10%In–Ti.

Characterization of photocatalysts

The Brunauer–Emmett–Teller surface area of the samples was measured using a Beckman–Coulter SA™ 3100 nitrogen adsorption apparatus. Prior to the surface area measurements, the samples were degassed at 423 K for 2 h. The pore size distributions of the samples were analyzed by the BJH method. The X-ray diffraction (XRD) analysis was carried out on a Bruker D2 phaser X-ray diffractometer with Cu K α as radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning rate of 1°/min. The data were collected in the 2θ range of 20–80° with a step size of 0.02°/s. UV–Vis diffuse reflectance spectra were measured with Perkin Elmer Lambda 750 spectrophotometer. BaSO₄ was the reference sample and the spectra were recorded in the range of 250–650 nm. Photoluminescence spectra were recorded on a Thermo Spectronic (Aminco Bowman Series 2) instrument with a Xe lamp as the excitation source at an excitation wavelength of 320 nm. The morphologies of the samples were analyzed by field emission scanning electron microscopy (Sigma, Zeiss). For preparation of specimen for FESEM analysis, the sample was first dispersed in a solvent. Then a drop of the suspension was placed on an aluminum foil and after drying at 80 °C overnight was gold coated. The elemental composition of the sample was characterized by EDS analysis equipped with the SEM instrument (LEO 1430 VP).

Photocatalytic activity studies

The photocatalytic reactions were carried out in a photo-reactor irradiated with a 500 W tungsten halogen lamp (Halonix, India), positioned at a distance of 15 cm away from the photoreactor. The feed mixture consisted of 25 ml of water and 1 ml of methanol with 0.2 g of photocatalyst. The photocatalyst was continuously dispersed in the aqueous methanol solution during irradiation period by stirring. The temperature of the reaction mixture was maintained at 298 K by a circulating water bath. Before illumination, the reaction mixture

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