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Enhanced photocatalytic hydrogen production activity of noble metal free MWCNT-TiO_2 nanocomposites

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ABSTRACT

Nanocomposite photocatalysts, MWCNT-TiO_2 were prepared by hydrothermal method. The photocatalysts were characterized by X-ray diffraction, Transmission electron microscopy (TEM), Raman spectroscopy, UV-Visible diffuse reflectance spectroscopy and photoluminescence (PL) spectroscopy to understand the crystal structure, morphology, and optical properties. The catalyst synthesis parameters such as calcination temperature and loading of MWCNTs were optimized for better hydrogen (H_2) production in 5 vol% glycerol aqueous solution under UV-visible light irradiation. Among the prepared nanocomposites, 0.1 wt% CNT loaded TiO_2 calcined at 450 °C for 2 h showed the highest H_2 production rate of 8.8 mmol g^{-1} h^{-1}. This higher H_2 production rate obtained can be ascribed to effective utilization of the photo generated electrons and holes for redox reactions.

Introduction

In 21st century, eco-friendly, clean energy sources are necessary to meet the global energy demand with reduced fossil fuel dependence and coupled environmental damage. In this connection, generating H_2 through photocatalysis process using environmentally benign renewable energy sources is the best choice. Hydrogen is the best alternative fuel over the other fossil fuels as it is clean and eco-friendly as combustion of it produces only water.

Titanium dioxide (TiO_2) is one of the potential strategic semiconductor for the photocatalytic water splitting due to its high chemical stability, favourable energy band structure, ready availability, inexpensive and non-toxic nature [1]. However, TiO_2 suffers from some serious disadvantages such as (i) ability to absorb only UV light covering very small (<5%) portion of solar light, (ii) backward reactions and (iii) rapid recombination of electron-hole pairs which limit the photocatalytic H_2 production efficiency. In order to overcome these problems, TiO_2 has been modified by many methods such as surface modification with organic materials [2], band gap modification by metals [3], non-metals [4,5], carbon based materials [6–8], semiconductor coupling [9], creation of oxygen vacancies and dye sensitization [10].

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Recently, one dimensional nanostructured (1-D) materials for instance nanorods, nanotubes and nanowires are found to be advantageous in photocatalysis. This is due to their unique properties such as high surface area and high aspect ratio, which offer easy way for transferring of ions, electrons, photons, gases and fluids [11,12]. Carbon nanotubes (CNTs) are the most promising 1-D nanomaterials used in photocatalysis, sensors and dye sensitized solar cell applications [13–15] due to favourable optical and electrical properties [16]. CNTs combined with TiO_2 make it a potential candidate for various applications [17–20] specifically for photocatalytic water splitting [21]. CNT-TiO_2 nanocomposites enhance the H_2 production by electron transfer from TiO_2 to CNTs, which promotes charge separation and reduces the chance of recombination [22,23].

Several studies have been carried out on CNT-TiO_2 nanocomposites for enhancing the H_2 production with added co-catalyst such as Pt, Pd etc. Kedai et al. prepared MWCNT-TiO_2 nanocomposite by hydrothermal method and then photodeposited it with Pt. The synthesized Pt-deposited nanocomposite was tested for photocatalytic H_2 production activity in visible light (250 W Xe-lamp) with triethanolamine (TEOA) as sacrificial agent [24]. In the same way, Yuvaraja et al. reported Pt@MWCNT-TiO_2 ternary hybrid composite synthesized by sol-gel technique for H_2 production in the UV-visible light (450 W Hg-lamp) using Na_2S and Na_2SO_3 as sacrificial reagents [25]. There are only few reports on H_2 production using CNT-TiO_2 nanocomposites without expensive co-catalysts such as Pt, Pd etc. Haopeng et al. showed improved photocatalytic H_2 production activity by TiO_2 nanotube/MWCNTs composites, without any noble metal co-catalysts, prepared by hydrothermal method under UV-Visible light (500 W Xe-lamp) using Na_2S and Na_2SO_3 as sacrificial reagents [26]. Alicia et al. reported mesoporous CNT/TiO_2 catalyst for H_2 production in a flow type cylindrical reactor under UV-visible light irradiation [27]. Recently, Wei et al. hydrothermally prepared carbon modified mesoporous TiO_2 catalyst with polyacrylate as the carbon source. They confirmed the increase in catalyst surface area while increasing calcination temperature upto 400 °C [28]. Cheng et al. reported a carbonaceous TiO_2 catalyst for removal of RhB dye under solar light [29]. Previously, our research group reported single-step preparation of carbon nanotubes and nanohorns/TiO_2 nanohybrids and synthesis of purified CNTs/TiO_2 nanotube (TiNT) nanohybrids by simple impregnation method. These catalysts showed higher photocatalytic H_2 production rate compared to TiO_2 under solar irradiation [22,30]. This improved photocatalytic activity on the hybrid catalysts is due to better surface interaction between TiO_2 and MWCNTs which enables charge carrier separation and transfer of electrons onto the surface active sites for redox reactions. However, crystallinity of TiO_2 and surface interaction between TiO_2 and MWCNTs can be further improved by other synthesis strategies such as hydrothermal method. Even though hydrothermal method is a well established, important synthesis method, parameter such as calcination temperature which affect the crystallinity and surface interaction between MWCNTs and TiO_2 were not thoroughly studied. Also, there is an escalating attention on the utilization of biomass derived products such as glycerol, ethanol and methanol etc. as sacrificial agents for photocatalytic water splitting [22,31,32]. Recently, Beltranet et al. detailed about use of biomass derived alcohols such as ethanol and methanol as sacrificial reagents in the H_2 production employing hierarchical MWCNTs/Pd@TiO_2 as the catalyst [33].

The present work is aimed at development of noble metal free CNT-TiO_2 nanocomposite catalysts by hydrothermal method for enhanced H_2 production under UV-visible light using 5 vol% aqueous glycerol as sacrificial agent. Glycerol is a primary by product in biodiesel production and it corresponds to approximately 10% of total biodiesel production in the world [34]. Since this work is a basic research for the efficient production of H_2 from solar water splitting, the cost and economic nature of the sacrificial regent was not taken into account. Calcination temperature of the samples and effect of CNTs was optimized for the better H_2 production activity. The catalysts were characterized for structural, morphological, and optical properties to understand the beneficial effect of MWCNTs on H_2 production.

Experimental details

MWCNTs/TiO_2 nanocomposites were synthesized by hydrothermal method. In a typical synthesis process, 1 g of TiO_2 and 0.1 wt% of MWCNTs were dispersed in 10 M NaOH aqueous solution and the mixture was transferred into a Teflon-lined autoclave and heated to 130 °C for 20 h in hot air oven. The obtained precipitate was washed with 0.l M HCl and distilled water. The washing process was repeated three times and finally the catalyst was dried at 100 °C overnight. The resulted product was calcined at different temperatures (350, 400, 450 and 500 °C) for 2 h. In the similar manner, MWCNTs/TiO_2 composites with different weight percentages of MWCNTs were also prepared. The details of the different catalysts prepared and their codes are given in Table 1. Materials used for preparation of catalysts, details of characterization techniques and the procedure followed for photocatalytic hydrogen production were given in supplementary information.

Results and discussion

Structural characteristics

Powder X-ray diffraction patterns of MWCNTs, 2MT-350, 2MT-400, 2MT-450, 2MT-500 and TiO_2 photocatalysts are presented in Fig. 1a. In MWCNTs, the peaks located at ~25 and 42.8° are assigned to (002) and (100) planes of carbon nanotubes (JCPDS 26-1079). 2MT-350, 2MT-400, 2MT-450 and TiO_2 displayed diffraction peaks at $2\theta = 25.3$, 37.8, 48, 53.8, 54.9, 62.5, 68.1, 69.7 and 75.2° corresponding to (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of anatase phase (JCPDS 21-1272). Further, the magnified XRD pattern of 2MT–500 catalyst is shown in Fig. 1b. In the 2MT-500 catalyst, peak intensities significantly decreased and additional small peaks appeared at 2θ values, 9.8, 24 and 28° corresponding to (200), (110) and (310) planes of sodium titanate which may be formed due to reaction of the base (NaOH) with TiO_2 [35,36]. In all the