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Shape dependence structural, optical and photocatalytic properties of TiO_2 nanocrystals for enhanced hydrogen production via glycerol reforming

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ABSTRACT

Herein, we demonstrate the effect of TiO_2 nanocrystals shapes on the structural, optical and photocatalytic properties for solar hydrogen (H_2) production in aqueous glycerol solution. Titanium dioxide (TiO_2) with different shapes such as nanotubes (TNT), nanorods (TNR) and nanosquares (TNS) were chosen and their photocatalytic performances were evaluated under similar conditions. It was observed that the TNT photocatalyst showed 1.5 and 2.0 folds enhanced H_2 production rate compared to TNR and TNS photocatalysts. Glycerol in water undergoes direct oxidation with in-situ generated holes to produce H^+ in aqueous solution which in-turn accepts pair of electrons to generate H_2 gas only. The catalytic performance is in good correspondence with the photocurrent density of the respective nanostructures in the following order TNT > TNR > TNS. The BET surface area of TNT displayed the improved adsorption of glycerol and its intermediates as compared to other catalysts. Thus, the enhanced photocatalytic activity of TNT was attributed to its synergistic properties owing to their peculiar one dimensional (1-D) nanotubular shape with active sites both interior and exterior surfaces. It enhanced the electron-pair lifetime and more efficient charge separation in TNT compared to TNR and TNS.

1. Introduction

The increase in energy supplies to operate electronic gadgets in domestic applications and automotive sectors consume massive energy derived from fossil fuels. The increasing energy crisis and societal demand for sustainable energy technologies to overcome environmental pollution arising from fuels become more important with respect to growing world population. In order to circumvent these problems, renewable and environmentally benign alternative energy resources are critically needed [1–4]. Owing to its high combustion energy and zero emission, hydrogen has always been considered as a potential alternative primary fuel as well as an energy carrier for future energy supply due to the fact that it can yield 120 MJ/Kg energy the highest amount of energy compared with other resources [5–8]. In this concern, the research advances in the hydrogen production have mainly focused on development of processes and catalysts. Thus, the idea of photocatalytic water splitting for producing hydrogen has been facilitated [9,10]. Water splitting into gaseous hydrogen (H_2) and oxygen (O_2) using semiconductor catalysts activated by solar light is one of the most promising technologies for producing cleaner and sustainable route for generation of chemical fuel. Various attempts have made to the design and development of titanium dioxide (TiO_2) photocatalyst for efficient H_2 generation. Several reports exist on size-dependent properties of TiO_2 for enhanced H_2 production. Nevertheless, only a very few studies have been focused on the shape-dependent properties of TiO_2 nanocrystals on H_2 evolution via photocatalytic process.

Over the past few decades, significant research efforts have been dedicated to the design of TiO_2 photocatalyst for efficient H_2 generation and several reports have been focused on effective preparation methods for biphasic nanostructured TiO_2 which often lead to synergistic photocatalytic H_2 production higher than that of bulk TiO_2 (P-25) [11–13]. Recently, our group explored a high rate of H_2 production ~99,823 μmol h^{-1} g^{-1}_{cat} under solar light irradiation and this enhancement of H_2 production can be attributed to high dispersion of catalyst in aqueous solution and nano-size effects of CuO/TiO_2 nanotube composite which results in the improved light absorption and charge

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carrier transfer at the catalyst surface-interface [14]. Based on our expertise, several efficient photocatalysts were developed and utilized for H_2 generation under solar/UV-light irradiation [14–21].

Generally, the structure and shape of photocatalysts depends on the steps of the synthesis method used. For example, different temperatures, surfactants and pH value of the synthesis can significantly influence on the control of shape and dimensionality and produce different crystal size, shape and structure [19,20]. On the other hand, it is believed that the catalytic properties may also strongly depend on the crystal size and shape of the photocatalyst used in the process. In literature, most of the studies including our recent reports have mainly focused either one or two particular shapes of photocatalysts for H_2 production. To the best of our knowledge, only very few studies have reported the effects on shape dependent properties of TiO_2 nanocrystals for H_2 evolution. For example, Yun et al. [22] have demonstrated the shape effects of anatase TiO_2 nanospheres and nanorods for H_2 evolution from aqueous ethanol solution under UV light irradiation. They found that Pt/TiO_2 nanorods generated 1.6 folds more H_2 gas than spheres.

Very recently, Camposeco et al. [23] investigated on the properties of TiO_2 nanomaterials with different structures and shapes for degradation of organic pollutants and they found that the photocatalytic activities for methylene blue and methyl orange degradation strongly depend on the various kind of TiO_2 nanostructures i.e. nano-tubes, nanofibers, nanowires and nanoparticles respectively, showing a strong relationship between their structure and the medium. It was also reported that the shape of TiO_2 will also affect the water splitting performance, by varying the charge transfer ability. Grimes and co-workers [24–27] prepared and examined the use of TiO_2 nanotube arrays for photoelectrochemical (PEC) water splitting, which greatly benefits from the nanotubular architecture with superior electron lifetimes that enhances the charge separation efficiency.

However, due to the lack of required information, it is necessary to investigate a specific work that can reveal the different shape-dependent properties of photocatalyst for effective H_2 production. Hence, new insights are provided to support the effect of the different shapes of TiO_2 nanocrystals for solar H_2 production. Herein, we delineate the comparative studies on effect of different shapes (one and two dimensional nanostructures) on the structural, optical and photocatalytic properties of TiO_2 for solar H_2 production via glycerol reforming. Thus, TiO_2 with different shapes such as nanotubes and nanorods were prepared by hydrothermal method at 130 °C and 180 °C followed by heat-treatment of dried powder at 350 °C and 500 °C, respectively. A commercial TiO_2 powder with nanosquares shape is used. This study emphasizes a correlation between the structural feature of the catalyst and their photocatalytic activity under solar light irradiation. In addition, a plausible mechanism for H_2 generation under solar light irradiation by using different nanostructured TiO_2 photocatalysts is proposed.

2. Experimental

Titanium dioxide (TiO_2 P-25) was procured from Degussa Corporation, Germany denoted as nanosquares (TNS). TiO_2 (anatase 99%, LAB) and all other chemicals of A.R grade supplied by Merck, India were used without any further purification. De-ionized water (100%, battery grade, LIMRA, Kadapa, India) was used for all the photocatalytic experiments.

In a typical hydrothermal synthesis of hydrogen trititanate nanotubes, anatase TiO_2 particles (2.5 g) were dispersed in 10 M sodium hydroxide solution (200 mL) heated at 130 °C for 20 h in a Teflon-lined autoclave (capacity 250 mL). The obtained product was washed thrice in the following order, de-ionized water, 0.1 M HCl solution and ethanol. The white powder dried at 80 °C for 12 h was placed in a ceramic boat and calcined at 350 °C for 5 h, and the obtained catalyst is denoted as TNT. In a typical synthesis of hydrogen trititanate nanorods, in the above procedure the hydrothermal treatment and calcination temperature are increased to 180 °C for 20 h and 500 °C for 5 h, respectively and the obtained catalyst is denoted as TNR.

The crystalline nature of the obtained photocatalysts was confirmed using the powder X-ray diffraction (PXRD) (Bruker, D8 ADVANCE). The shape and size of the photocatalysts were characterized by transmission electron microscopy (TEM, FEI Tecnai F20ST). The optical absorption properties of the catalysts were tested using the diffuse reflectance (DR) UV–Visible spectroscopy (GBC, Cintra 10e). The surface area and porous nature of the catalysts are estimated by using the N_2 adsorption-desorption measurements (Micromeritics, ASAP 2020).

The PEC measurements were performed in a conventional three electrode system with a Pt-wire as the counter electrode and Ag/AgCl (in saturated KCl) as a reference electrode. PEC measurements were recorded using a Biologic SP-300 electrochemical workstation with A 250 W Xe arc lamp (Oriel, USA) as the light source. A 0.1 M Na_2SO_4 aqueous solution was used as the electrolyte solution. The working electrode was prepared by mixing 50 mg of the photocatalyst with 150 mL of PEG (mol wt 400) and 125 mL of ethanol was used to make slurry. It was then coated on a 2.5×2.5 cm^2 fluorine-doped tin oxide (FTO) glass substrate with an active area of about 1×1 cm^2 by the doctor-blade method using scotch tape as a spacer. It was dried in air and then annealed at 350 °C for 45 min.

The photocatalytic activity tests were carried out in a quartz reactor (top loading port) sealed with a gas tight rubber septum. Typically, 5 mg of catalyst was dispersed in 50 mL of 5 vol% aqueous glycerol solution and stirred for 30 min in dark condition. The gas present in the reactor was evacuated followed by purging with N_2 gas to obtain an inert atmosphere. The photocatalytic activity experiments were performed under natural solar light irradiation (1.15×10^5 lx) and generated H_2 gas was analyzed by using Gas Chromatograph (Shimadzu GC-2014), equipped with thermal conductivity detector (TCD) and Molecular Sieve/5A column, at 70 °C using N_2 as the carrier gas. The stability of the catalyst was examined by recyclability studies [20].

3. Results and discussion

3.1. Structural characterization

3.1.1. Shape and surface analysis

Different shapes and structure of the photocatalysts were investigated by TEM analysis and the images are shown in Fig. 1. The agglomerated nanocrystals is shown in Fig. 1a and the HRTEM image of Fig. 1b displays nanosquares (TNS) with all three dimensions in the nanoscale, the length and breadth in the order of 23 and 28 nm. The SAED shown in Fig. 1c shows the polycrystalline nature of TNS which is in good agreement with the biphasic anatase-rutile structure obtained in the X-ray diffraction pattern. Similar observations have also been reported in the literature [28–30]. Fig. 1d shows the 1-D nanotubular nature of the TNT with open ends (hollow tube). The HR-TEM image (Fig. 1e) clearly indicates that the inner, outer diameters and length of the TNT nanotubes are between 8–12, 3–5 and 100–200 nm, respectively. The polycrystalline nature of the SAED pattern (Fig. 1f) confirms the presence of biphasic anatase-rutile structure in TNT catalyst [20,21].

The low-resolution TEM image of TNR sample (Fig. 1g) shows rod-like shape with nanocavities. Whereas, at higher magnification (Fig. 1h) it could be clearly seen that the surface of TNR has nanocavities with different shapes such as circular, rectangular and elliptical. The observed SAED pattern (Fig. 1i) confirms the presence of anatase and TiO_2 (B) phases. In our earlier report, it was observed that the TiO_2 nanorods change its crystal phase and nanocavities upon heat treatment [19]. Xu et al. [31] also explained the crystal phase transformation and damage of 1-D shape upon thermal treatment of titanate nanotubes at 400 °C.