



Preparation and characterization of metals supported on nanostructured TiO₂ hollow spheres for production of hydrogen via photocatalytic reforming of glycerol

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ABSTRACT

Nanostructured TiO₂ hollow spheres (THS) were prepared via a simple hydrothermal method with titanium butoxide, ethanol, urea, and ammonium sulphate. The effects of Ti/ethanol, and reflux temperature on the morphological properties of the nanostructured THS were investigated. An impregnation method was subsequently employed to load metals such as Cu, Co, Cr, Ag, and Ni on the optimized THS, followed by calcination in H₂/N₂ at 450 °C for 4 h. The morphological properties of the prepared samples were characterized by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and ultraviolet-visible spectroscopy (UV/vis). The SEM and TEM pictures showed that the Ti/ethanol ratio of 1:10 resulted in the formation of uniform hollow spheres. The XRD spectra revealed that phase transformation took place as the reflux temperature was increased, with pure anatase TiO₂ hollow spheres being formed at 200 °C. The BET surface areas of the calcined photocatalysts were in the range of 80.6–116 m²/g⁻¹. The UV/vis spectra of the photocatalysts showed that loading of transition metals reduced the band gap of the THS. The activities of the prepared catalysts were tested for hydrogen production via photocatalytic reforming of glycerol under solar irradiation. The improved hydrogen evolution from photocatalytic reforming of glycerol was attributed to: the high surface area which enhanced the adsorption of glycerol onto the surface of photocatalysts; high crystallinity and the reduced band gap which improved the solar light harvesting; the hollow chamber within the TiO₂ spheres which produced multiple reflection of the light harvested, thus producing efficient electron/hole pair formation; and the detailed composition of the solids retarded the electron/hole recombination by trapping the electrons generated during the photo excitation of the photocatalysts, and thereby promoted their activity.

1. Introduction

The increase in population has raised alarms regarding energy demands, and most of the world's energy is produced from non-renewable energy sources such as fossil fuels. However, it has been predicted that these fossil fuels will be depleted in the near future due to the increased rate of their exploitation. Therefore, due to the inevitable depletion of the fossil fuels, and the global climate change which is caused by the combustion of these fuels, research has been directed towards finding alternative energy sources which are renewable and environmentally friendly [1,2]. Hydrogen is recognised as an alternative ecologically friendly energy vector due to its high combustion energy of 120 MJ/kg, which is higher than any other source of energy; and also because of it

zero percentage carbon emissions [3,4]. Currently, most of the world's sustainable hydrogen is being produced from commercial processes such as pyrolysis, steam reforming, and steam gasification using renewable biomass and water as sources of hydrogen [5–7]. These commercial processes however, require large amounts of energy which makes them costly, and they tend to leave a large carbon footprint on the environment. Photocatalytic production of hydrogen from renewable biomass such as glycerol, over semiconductor photocatalysts, under solar irradiation is a potential alternative process which is environmentally friendly, not costly, and easy to set up and operate [8–11]. Titanium dioxide, TiO₂ is widely employed as catalyst since it is low cost, non-toxic, biologically and chemically stable, and it is resistant to photocorrosion. Unfortunately, it has been reported

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previously that TiO₂ showed poor activity during water splitting under solar irradiation because of its wide band gap of 390 nm [12]. This large band gap limits the activity of TiO₂ to ultraviolet (UV) irradiation, which only makes up < 6% of the solar spectrum, whilst visible light makes up ~40% of the solar spectrum. Furthermore, the low activity of the pure TiO₂ during the hydrogen production was attributed to the accelerated recombination of photogenerated electron/hole pairs and the reverse reaction of the intermediates produced [13]. Gholipour et al., [14] reported that incorporation of metals or metal oxides with TiO₂ as co-catalysts can enhance the activity and retard the electron/hole recombination during photocatalytic water splitting.

Over the past few decades, TiO₂ materials with varying nanostructures and morphologies have been successfully prepared, and hollow spheres of nanostructured TiO₂ have received a lot of attention because of their potential application as photocatalysts/supports; their excellent photocatalytic ability is attributed to the multiple light reflection which occurs inside their hollow chambers, and their ease of separation from the reaction mixture [15–17]. The hollow spheres of TiO₂ have been prepared using template-assisted sacrificial methods; however, the removal of these templates is a very complex and energy consuming process [18]. Recently, these hollow spheres TiO₂ have been successfully prepared using template-free methods, which makes ease of handling and upscaling practical

[19] Wang et al., [20] successfully prepared TiO₂ hollow spheres (THS) with enhanced photocatalytic activity of hydrogen production via a facile, template-free hydrothermal method. In this paper, we report on the successful preparation of THS via a simple one-pot hydrothermal method; and the loading of transition metals onto the surface of the THS by incipient wet impregnation. The activities of the prepared catalysts for the photocatalytic production of hydrogen from glycerol reforming have been assessed. This study gives new insights into the incorporation of transition metals into the surface of the THS in order to enhance the photocatalytic activity for improved hydrogen evolution.

2. Experimental

2.1. Preparation of M/THS photocatalysts

All the reagents used in this study were of analytical grade and were used as received. The nanostructured THS were successfully prepared by a simple one-pot hydrothermal method. First, ammonium sulphate (12 g) and urea (5 g) were dissolved in desired mass of absolute ethanol in a reaction flask, under vigorous stirring for 45 min. Titanium butoxide of desired mass was added dropwise to the resulting mixture under vigorous stirring, and the whole subsequently aged overnight. The resulting precipitates-transparent liquid mixture was then refluxed at desired temperatures for 5 h, and subsequently allowed to cool naturally to room temperature. The precipitates were filtered, and then washed three times with high purity distilled water, followed by washing five times with absolute ethanol. The resulting powders were oven-dried overnight at 120 °C. The Ti/ethanol ratio and reflux temperature were varied in order to investigate their effect on the formation of THS. The incipient wetness impregnation method was used to load transition metals, Ni, Cu, Co, Ag, or Cr onto the surface of the THS; and the impregnated samples were calcined at 450 °C in flowing 20% H₂/N₂ for 5 h. The prepared samples were denoted as: plain THS, THS@450C, Ni/THS, Cu/THS, Co/THS, Ag/THS, and Cr/THS.

2.2. Structural characterization

The crystal phase structure of the prepared THS and M/THS photocatalysts were analyzed by X-ray power diffraction (Bruker AXS D8 Advance). The XRD patterns were recorded at room temperature with scanning speed of 2° min⁻¹ using Co K_α radiation (λ = 1.8 nm) from a 40 kV X-ray source and diffracted beam monochromator, operated at 35 mA. Scanning electron micrograph (SEM) images were obtained

using an FEI NOVA NANOSEM 200. The samples were deposited on a sample holder with a piece of adhesive tape in order to make them conductive, and subsequently inserted in the SEM. Transmission electron microscopy (TEM) images were recorded using the LEO 912 OMEGA TEM, operating at 120 kV, equipped with Proscan CCD camera for digital image acquisition. The images were analyzed using the Soft Image System (SIS) software. The Autosorb-I (Quantachrome) equipment was used to obtain the Brunauer-Emmett-Teller (BET) surface areas and porosity properties of the photocatalysts by N₂ adsorption at -196 °C. The GBC UV-vis Cintra 10e spectrophotometer was employed to record the UV-vis diffuse reflectance spectra (DRS) at room temperature in the range of 300–700 nm. The photoluminescence (PL) emission and excitation (PLE) properties of the prepared materials were probed using an Edinburgh Instrument FS920 photoluminescence spectrometer with an excitation wavelength of 350–380 nm, using Xe light as the light excitation source. The widths of the emission slit and excitation slit were both 10 nm.

2.3. Photocatalytic activity

The photocatalytic hydrogen production tests were performed in a 150 mL quartz reactor under solar irradiation. First, 50 mL of solution containing 5% (v/v) glycerol was prepared with high purity distilled water, and 100 mg prepared samples were used as the photocatalyst. The glycerol solution, together with the prepared photocatalyst was added into the quartz reactor which was sealed with a silicone rubber septum. Prior to solar irradiation, the slurry in the reactor was evacuated for 30 min and bubbled with helium for 50 min in order to completely remove the dissolved oxygen and to ensure that the reactor was operating in an anaerobic condition. The catalyst was kept in suspension by continuous magnetic stirring during the entire period of the experiment. The analysis of H₂ evolved was conducted every 1 h for 4 h by extracting 0.5 mL of the gas sample from the reactor and subsequently injecting it into the gas chromatograph (Shimadzu GC-2010) using He as a carrier gas.

3. Results and discussion

3.1. SEM analysis

Fig. 1 shows the SEM images of the plain THS prepared from different titania/ethanol ratios. The overall morphology shown in high-magnification SEM images [Fig. 1(a)-(b)] revealed that the samples consisted of uniform spherical particles with diameters in ranges 60–125 nm and 86–115 nm, respectively. Furthermore, a rough surface of the spheres observed from Fig. 1(a)-(b) indicated that the aggregation of numerous spherical and irregular shaped TiO₂ nanoparticles of 60–125 nm and 86–115 nm, respectively, took place via self-assembly to form hollow spheres with diameter of 0.6–1.25 μm. Moreover, it was observed that a higher concentration of the titania precursor [Fig. 1(a)] lead to formation of larger spherical particles with rougher surfaces due to a higher growth rate, although the particles appeared to have agglomerated into clusters. When the titania/ethanol ratio was increased to 1:10, uniform spherical particles were achieved. However, no uniform spherical particles were observed from Fig. 1 (c); which suggests that the ratio of titania-solvent plays an important role in the formation of hollow spheres [20,21]. Therefore, the optimum titania/ethanol ratio was found to be 1:10.

Fig. 2 shows the SEM images of prepared samples using the titania/ethanol optimum ratio and which underwent hydrothermal processes at different temperatures for 5 h. It is observed that the prepared samples retained their spherical structure, even after undergoing hydrothermal treatment at 200 °C, but the particle size increased along with some aggregation. However, Fig. 2(a) shows that the hydrothermally treated aggregates at 80 °C appear to be loosely packed, but as the hydrothermal temperature is increased, the aggregates become compacted.

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