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Short Communication

Infrared radiation active, novel nanocomposite photocatalyst for water splitting

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ARTICLE INFO

Article history:

Received 7 May 2014

Received in revised form

7 July 2014

Accepted 22 July 2014

Available online 14 August 2014

Keywords:

IR active photocatalyst

Ag₂OTiO₂

Sub-band gap excitation

Photolysis

ABSTRACT

In this report, we investigated an infrared photon active catalytic system for the conversion of solar energy into chemical energy in which we introduced an effective “Dark Photocatalyst” for photolysis of water. The Ag₂O/TiO₂ composite catalyst containing 28% of silver and 72% of titanium was synthesised by a simple chemical deposition method. The catalyst was found to be active in the infrared region of the solar spectrum or in the dark and hydrogen production was demonstrated for the first using low-energy 800–1200 nm IR radiation. Sub-band gap phonon assisted multi-photon excitation is proposed for the observed infrared photocatalytic activity of Ag₂O/TiO₂ composite.

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Introduction

The concept of electrochemical photolysis of water by single-crystal TiO₂ under UV light was first reported with analogy to natural photosynthesis in 1972 [1]. Water splitting into hydrogen is an effective method of converting solar energy into chemical energy and hydrogen is a promising alternative to fossil fuels since it contains 3.4 times more energy on a weight by weight basis compared to gasoline [2]. TiO₂ is the most widely used photocatalytic material [3]. However, TiO₂ absorbs mainly high energy photons in the UV region of the solar spectrum and to develop TiO₂ for practical applications, band gap engineering is required to alter the band-energy of

TiO₂. Hence, finding novel nanostructured semiconductors that would absorb lower-energy photons such as visible and infrared (IR) regions of the solar spectrum is imperative for pragmatic applications of photocatalysts. Many attempts have been made to utilise the visible region of the solar spectrum of TiO₂ photocatalysts through impurity doping, metallisation and sensitization [4–7]. However no attempt has been made to use the IR region of the solar spectrum for photolysis of water. Advantages of such a system are that IR radiations are available from the sunset to sunrise and solar spectrum consists of 47% IR radiation [8]. In this investigation, we report a new concept where the photocatalyst will be able to absorb low-energy IR radiation by phonon assisted multiphoton-photoexcitation and generates active

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<http://dx.doi.org/10.1016/j.ijhydene.2014.07.118>

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electron–hole (e^- – h^+) pairs that will participate in the water splitting reaction generating H_2 . We demonstrate that the Ag_2O/TiO_2 composite is able to photolyse water by absorbing low-energy IR photons and show that the process involves sub-band gap excitations and a possible mechanisms for the photoactivity of Ag_2O/TiO_2 is proposed.

Experimental section

Ag_2O/TiO_2 composite photocatalyst was synthesised by controlled hydrolysis of $AgNO_3$ in the presence of TiO_2 . A mixture containing TiO_2 (P25 Degussa) (2% w/v) in 50 ml of 0.04 M aqueous $AgNO_3$ (BDH analytical grade) was stirred for 30 min followed by the addition of a stoichiometric amount of 33% ammonia solution for the complete conversion of $AgNO_3$ to Ag_2O . The resulting mixture was heated at 150 °C until the product is completely dry and the resultant powder was calcined at 250 °C for 30 min. As control, bare TiO_2 and Ag_2O were prepared in a similar manner without adding $AgNO_3$ and TiO_2 respectively and taken as control catalysts. For the photolysis experiment, finely ground 12.5 mg of Ag_2O/TiO_2 photocatalyst was dispersed in 20 ml of 10% methanol or deionised water and placed in a 25 ml borosilicate flask which was tightly sealed with a gas septum and irradiated with two IR emitting diodes (850 and 950 nm, ϕ 5 mm, 3.2 mW cm^{-2}) and the experiments were carried out in a dark room to avoid UV and visible light. The gases products of water splitting were analysed quantitatively using a Shimadzu gas chromatograph GC-9AM with a TCD detector with a packed charcoal column (which separates H_2 and O_2) using Ar as the carrier gas. External incident photon current conversion efficiency (IPCE) was measured using a Bentham PVE 300 1700 IPCE apparatus. UV visible spectrum was recorded in ShimadzuUV-2450 UV–VI spectrophotometer.

Results and discussion

When the catalyst was irradiated with IR source in 10% methanol solution, production of hydrogen was noticed (As we noted a rapid absorption of photoproducted H_2 on to Ag_2O/TiO_2 catalyst, the catalytic system was sonicated continuously during irradiation to separate H_2 from the catalyst surface). Hydrogen production rates of individual catalysts of TiO_2 , Ag_2O and Ag_2O/TiO_2 composite were investigated in air and argon saturated photolysis conditions and these results are given in Table 1. Hydrogen production rates of Ag_2O , TiO_2 and

Ag_2O/TiO_2 in 10% MeOH solution under air saturated conditions with the IR light source (3.2 mW cm^{-2}) were 0.17, 0.19 and 5.83 ml $h^{-1} g^{-1}$ respectively while for the same systems, hydrogen production rates were 0.56, 2.41 and 25.64 ml $h^{-1} g^{-1}$ respectively under argon saturated condition (a lower hydrogen production rate under air is due to capture of excited electron by oxygen.). The hydrogen production rate of Ag_2O/TiO_2 nanocomposite under air is about ~30 times more when compared to the hydrogen production of TiO_2 and Ag_2O under similar conditions. Under argon saturated conditions, hydrogen production rate is 10 and 50 times higher when compared to the hydrogen production rates of TiO_2 and Ag_2O respectively. As the irradiation light source for the above experiments were either a 850 or 950 nm light emitting IR diodes, it can be assumed that the photolysis of water with Ag_2O/TiO_2 catalyst was initiated by the absorption of IR photons. The observed higher hydrogen production rate for Ag_2O/TiO_2 catalyst compared to Ag_2O or TiO_2 alone indicates the existence of a synergic effect of both TiO_2 and Ag_2O in IR initiated catalytic activity of the Ag_2O/TiO_2 catalyst. Moreover, hydrogen production was observed for the same catalysts under similar photolysis conditions using deionised water and the hydrogen production rates of Ag_2O/TiO_2 , TiO_2 and Ag_2O are given in Table 1. As given in Table 1, the hydrogen production rate is higher with MeOH than H_2O due to capturing of excited holes by sacrificial MeOH resulting in enhanced charge separation.

Hydrogen was not observed when the photolysis experiments were carried with Ag_2O/TiO_2 catalyst in the absence of IR light or without Ag_2O/TiO_2 catalyst. Additionally, a very small amount of hydrogen production was observed when the irradiation was carried out with Ag/Ag_2O and Ag/TiO_2 composites under IR irradiation. Additionally no hydrogen was observed when sonication of pure water and 10% methanol in the presence and absence of IR radiation under air without Ag_2O/TiO_2 catalyst. Absence of formation of hydrogen under sonication of pure water and water-methanol mixture in air confirms that the sonolysis alone does not produce hydrogen and the observed hydrogen production with Ag_2O/TiO_2 catalyst is not due to a sonochemical reaction [9,10]. On the other hand, during thermal catalytic activity of Ag_2O/TiO_2 catalyst, a very low H_2 formation (fifty times less when compared to the yield of photolysis by the IR radiation) was observed only at 90 °C indicating that H_2 is not formed due to a thermal reaction. Further, the temperature rise due to IR irradiation and sonication is below 40 °C and hence H_2 production due to thermal reaction cannot be expected. These observations and the photolysis results presented above confirm the IR active photocatalytic activity of Ag_2O/TiO_2 catalyst.

Strong evidences for the IR response of Ag_2O/TiO_2 catalyst come from the investigation of spectral response and intensity dependence of catalytic activity Ag_2O/TiO_2 catalyst. Fig. 1(a) shows the IPCE measurements of the Ag_2O/TiO_2 films which were carried out in the presence of 10% methanol as an electrolyte and Pt as counter electrode in the 300–1100 nm region at a bias voltage of 200 mV. IPCE measurements of TiO_2 , Ag_2O and Ag_2O/TiO_2 which were carried out only in the 600–1100 nm region are also shown in Fig. 1(b–d) respectively for comparison purposes. As shown in Fig. 1(a), the IPCE spectrum of Ag_2O/TiO_2 shows a wide response from 300 to

Table 1 – H_2 yield by photolysis of 10% methanol and deionised water under IR irradiation per unit catalyst mass with total intensity of 3.2 mW cm^{-2} .

Catalyst	H_2 yield (ml $h^{-1} g^{-1}$)			
	10% Methanol		Deionised water	
	Under Ar	Under air	Under Ar	Under air
Ag_2O/TiO_2	25.64	5.83	2.41	0.176
TiO_2	2.41	0.19	0.55	0.04
Ag_2O	0.56	0.17	0.11	0.017

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