Available online at www.sciencedirect.com

**ScienceDirect** 

journal homepage: www.elsevier.com/locate/he



# Short Communication

# Infrared radiation active, novel nanocomposite photocatalyst for water splitting



HYDROGEN

# A. Gannoruwa<sup>a</sup>, K. Niroshan<sup>a</sup>, O.A. Ileperuma<sup>b</sup>, J. Bandara<sup>a,\*</sup>

<sup>a</sup> Institute of Fundamental Studies, Hantana Road, CP 20000, Kandy, Sri Lanka <sup>b</sup> Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka

#### 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 Ag<sub>2</sub>O TiO<sub>2</sub> 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  $Ag_2O/TiO_2$  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  $Ag_2O/TiO_2$  composite.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

The concept of electrochemical photolysis of water by singlecrystal  $TiO_2$  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].  $TiO_2$  is the most widely used photocatalytic material [3]. However,  $TiO_2$ absorbs mainly high energy photons in the UV region of the solar spectrum and to develop  $TiO_2$  for practical applications, band gap engineering is required to alter the band-energy of TiO<sub>2</sub>. 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 TiO<sub>2</sub> 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

\* Corresponding author. Tel./fax: +94 812 232 131.

E-mail address: jayasundera@yahoo.com (J. Bandara).

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

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

electron-hole (e<sup>-</sup>-h<sup>+</sup>) pairs that will participate in the water splitting reaction generating H<sub>2</sub>. We demonstrate that the Ag<sub>2</sub>O/TiO<sub>2</sub> 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<sub>2</sub>O/TiO<sub>2</sub> is proposed.

#### **Experimental section**

Ag<sub>2</sub>O/TiO<sub>2</sub> composite photocatalyst was synthesised by controlled hydrolysis of AgNO3 in the presence of TiO2. A mixture containing TiO<sub>2</sub> (P25 Degussa) (2% w/v) in 50 ml of 0.04 M aqueous AgNO<sub>3</sub> (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<sub>3</sub> to Ag<sub>2</sub>O. 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<sub>2</sub> and Ag<sub>2</sub>O were prepared in a similar manner without adding AgNO3 and TiO<sub>2</sub> respectively and taken as control catalysts. For the photolysis experiment, finely ground 12.5 mg of Ag<sub>2</sub>O/TiO<sub>2</sub> 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,  $\phi$  5 mm, 3.2 mW cm<sup>-2</sup>) 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 photoproduced  $H_2$  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<sub>2</sub>,  $Ag_2O$  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<sub>2</sub> and

Table 1 – H <sub>2</sub> 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 <sup>-1</sup> g <sup>-1</sup> )			
	10% Methanol		Deionised water		
	Under Ar	Under air	Under Ar	Under air	
Ag <sub>2</sub> O/TiO <sub>2</sub>	25.64	5.83	2.41	0.176	
TiO <sub>2</sub>	2.41	0.19	0.55	0.04	
Ag <sub>2</sub> O	0.56	0.17	0.11	0.017	

Ag<sub>2</sub>O/TiO<sub>2</sub> 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<sup>-1</sup> 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<sub>2</sub>O/ TiO<sub>2</sub> nanocomposite under air is about ~30 times more when compared to the hydrogen production of TiO<sub>2</sub> and Ag<sub>2</sub>O 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<sub>2</sub> and Ag<sub>2</sub>O 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<sub>2</sub>O/TiO<sub>2</sub> catalyst was initiated by the absorption of IR photons. The observed higher hydrogen production rate for Ag<sub>2</sub>O/TiO<sub>2</sub> catalyst compared to Ag<sub>2</sub>O or TiO<sub>2</sub> alone indicates the existence of a synergic effect of both TiO<sub>2</sub> and Ag<sub>2</sub>O in IR initiated catalytic activity of the Ag<sub>2</sub>O/TiO<sub>2</sub> 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<sub>2</sub>O are given in Table 1. As given in Table 1, the hydrogen production rate is higher with MeOH than H<sub>2</sub>O 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<sub>2</sub>O/TiO<sub>2</sub> catalyst in the absence of IR light or without Ag<sub>2</sub>O/TiO<sub>2</sub> catalyst. Additionally, a very small amount of hydrogen production was observed when the irradiation was carried out with Ag/Ag<sub>2</sub>O and Ag/TiO<sub>2</sub> 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<sub>2</sub>O/TiO<sub>2</sub> 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<sub>2</sub>O/TiO<sub>2</sub> catalyst is not due to a sonochemical reaction [9,10]. On the other hand, during thermal catalytic activity of Ag<sub>2</sub>O/TiO<sub>2</sub> catalyst, a very low H<sub>2</sub> formation (fifty times less when compared to the yield of photolysis by the IR radiation) was observed only at 90 °C indicating that H<sub>2</sub> is not formed due to a thermal reaction. Further, the temperature rise due to IR irradiation and sonication is below 40  $^\circ\text{C}$  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<sub>2</sub>O/TiO<sub>2</sub> 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<sub>2</sub>,  $Ag_2O$  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



Fig. 1 – IPCE of the cells, (a,d)  $Ag_2O/TiO_2$  nanocomposite, (b)  $TiO_2$ , (c)  $Ag_2O$  in 10% methanol electrolyte and the platinum counter electrode at bias voltage of 200 mV.

1100 nm with clear two responses at 350 and 850 nm. The sharp response at 350 nm corresponds to the direct excitation of electrons from valence band (VB) to the conduction (CB) of TiO<sub>2</sub>. The broad response in the visible-IR region could be easily assigned to the excitation of silver resonance plasmon and Ag<sub>2</sub>O particles by comparing the IPCE spectra of individual TiO<sub>2</sub>, Ag<sub>2</sub>O with Ag<sub>2</sub>O/TiO<sub>2</sub> shown in Fig. 1(a-d). As shown in Fig. 1(b),  $TiO_2$  shows a feeble response at 750 nm which is due to a sub-band gap excitation process of TiO<sub>2</sub> by IR radiation and can be attributed to the existence of sub-band gap states between the CB and VB arising from oxygen vacancies [11-13]. Similarly, the IPCE spectrum of Ag<sub>2</sub>O [Fig. 1(c)] shows a broad response in the VIS-IR region with a sharp response at 850 nm which can be attributed to surface plasmon resonance of Ag and  $Ag_2O$  [14–16]. Interestingly, the IPCE spectrum of  $Ag_2O/$ TiO<sub>2</sub> resembles to that of Ag<sub>2</sub>O with a broad spectral response in the VIS-IR region (a broad response at ~850 nm) indicating that the observed broad response of Ag<sub>2</sub>O/TiO<sub>2</sub> in VIS-IR regions arises due to surface plasmon resonance of Ag and Ag<sub>2</sub>O. As explained earlier, the IPCE response of Ag<sub>2</sub>O/TiO<sub>2</sub> catalyst spreads in the visible to IR regions with a clear enhanced response in the IR region of the solar spectrum. The clear IR response of the Ag<sub>2</sub>O/TiO<sub>2</sub> catalyst in the IPCE spectrum undoubtedly demonstrates the IR activity of the Ag<sub>2</sub>O/ TiO<sub>2</sub> catalyst in the 700 to 1100 nm region of the solar spectrum.

Optical properties of the Ag<sub>2</sub>O/TiO<sub>2</sub> catalyst have been examined and the results are presented in Fig. 2. The UV–VIS spectrum of TiO<sub>2</sub> shows an absorption threshold at ~380 nm due to direct band gap excitation while Ag<sub>2</sub>O shows an absorption band around 800 nm. The UV–VIS absorption spectrum of as prepared Ag<sub>2</sub>O/TiO<sub>2</sub> shows a featureless absorption starting from ~700 to 800 nm while just after irradiation with IR radiation in the presence of water, the catalyst turns to a black colour with absorption peaks at 350, 500 and 800 nm. The peaks at ~500 and 850 nm can be attributed to silver plasmon and Ag<sub>2</sub>O absorptions respectively. A band gap value of approximately 1.58 eV was determined and the value agrees well with the reported band gap E of ~1.5 eV for Ag<sub>2</sub>O [17,18]. Interestingly, the shape and the peak wavelength of the IPCE spectrum coincides with the optical absorption spectrum of  $Ag_2O/TiO_2$ , thus indicating that the photocurrent observed in the IR region is caused by the local surface plasmon resonance based excitation of the Ag and  $Ag_2O$  particles.

IR response of the Ag<sub>2</sub>O/TiO<sub>2</sub> catalyst was further confirmed by the investigation of intensity depended catalytic activity of Ag<sub>2</sub>O/TiO<sub>2</sub> catalyst. By comparing band gap energies of TiO<sub>2</sub> (3.3 eV) and Ag<sub>2</sub>O (1.58 eV) to energies of IR sources (1.30 and 1.45 eV), it can be inferred that the direct band gap excitation either in  $Ag_2O/TiO_2$ ,  $Ag_2O$  or  $TiO_2$  is not possible with IR radiation. If excitation to happen by IR radiation, it could arise only due to sub-band gap or multi-photon excitation. To prove the multi-photon excitation in Ag<sub>2</sub>O/TiO<sub>2</sub>, we studied the excitation intensity dependence on the H<sub>2</sub> yield of the Ag<sub>2</sub>O/TiO<sub>2</sub> nanocomposite catalyst and the results are shown in Fig. 3. As shown in Fig. 3, the variation of the H<sub>2</sub> yield with light intensity was found to be exponential where in the plot of ln[H<sub>2</sub> yield] Vs, ln(Intensity), the fitting results gave a slope of 1.78 (inset in Fig. 3). A slope of 1.78 in the plot of ln[H<sub>2</sub> yield] Vs, ln(Intensity) indicates a non-linear process that involves multi-photon electron excitation in Ag<sub>2</sub>O/TiO<sub>2</sub> [19]. This type of multi-photon excitations have been reported for several other oxides [9-10,12] and nitrides [20] and the



Fig. 2 – UV–VIS spectra of  $Ag_2O/TiO_2$  nanocomposite  $Ag_2O$  and  $TiO_2$ .



Fig.  $3 - H_2$  yield at different IR intensities. Inset is the plot of ln [H<sub>2</sub> yield] Vs. ln (Intensity).

observed multi-photon excitation has been attributed to ONF induced – Phonon assisted IR or sub-band gap response [21,22]. In the ONF-phonon assisted process, it has been postulated that the ONF generated at the nanostructures, excite the coherent phonons in the nanostructures forming virtual excition-phonon-polariton and these quasi particles can excite the electrons to the phonon level and successively to the CB [22]. These ONF with the assistance of phonons could generate exciton-phonon-polariton in both TiO<sub>2</sub> and Ag<sub>2</sub>O. As the energy required for the process is very low, IR radiation can excite electrons from VBs of TiO<sub>2</sub> and Ag<sub>2</sub>O to these sub energy levels and with a sequence of steps, an electron can be excited from VBs to the CBs of TiO2 and Ag2O. Such an approach requires the existence of proper electronic states whose energy positions lie within the band gap. These states could be localized electronic states (LS) of intrinsic defects.

Based on these observations and results, we initially proposed a multi-photon photocatalytic process for  $Ag_2O/TiO_2$  composite catalyst. In multiphoton photocatalytic process, electrons and holes could generate and trap/de-trap in subband gaps of the catalyst by IR photons with the help of tuneable surface Plasmon resonance of Ag and/or Optical Near Field (ONF) induced – phonon assisted process. The detailed proposed mechanism and the microstructures of  $Ag_2O/TiO_2$ ,  $TiO_2$  and  $Ag_2O$  will be discussed in a future article.

# Conclusion

In conclusion, IR photon initiated  $H_2$  production via photolysis of  $H_2O$  was demonstrated for the first time by using a  $Ag_2O/TiO_2$  photocatalyst. Photolysis reaction seems to involved sub-band gap or multiphoton processes where ONF-phonon assisted excitation mechanism is proposed which should be verified by further investigation. The proposed ONF-phonon assisted system for the production of  $H_2$ could be a promising artificial system for efficient harvesting of solar energy, specially the IR region of the solar spectrum. The present IR photon harvesting system can be applied not only for the photolysis of water but also for photodegradation of pollutants and conversion of solar energy into electrical energy.

## Acknowledgements

Financial support from NRC, Sri Lanka (NRC 07 – 46) is highly appreciated. It should be a pleasure of acknowledge Prof. Mowafak Al-Jassim (NREL, Colorado, USA) for providing SEM and TEM images and to Mr. Buddi Ariyasinghe (Research Institute of Electronics, Shizuoka University, Japan) for XPS analysis. We wish to thank Mr Dammika Prasad Wijethunga (IFS, Kandy Sri Lanka) for helping us in assembling the IR source and Ms. Darshani Aluthpatabendi (IFS, Kandy Sri Lanka) for the technical assistance given during this study. Finally we would like to thank Prof. A. Nanayakkara (IFS, Kandy Sri Lanka) for his valuable comments.

#### REFERENCES

- Fujishima A, Honda K. Electrochemical photolysis of water at a semiconductor electrode. Nature 1972;238:37-8.
- [2] Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Environmental applications of semiconductor photocatalysis. Chem Rev 1995;95:69–96.
- [3] Lin C-J, Lu Y-T, Hsieh C-H, Chien S-H. Surface modification of highly ordered TiO<sub>2</sub> nanotube array for efficient water splitting. Appl Phys Lett 2009;94:113102.
- [4] Dunnill CW, Ansari Z, Kafizas A, Perni S, Morgan DJ, Wilson M, et al. Visible light photocatalysts—N-doped TiO<sub>2</sub> by sol-gel, enhanced with surface bound silver nanoparticle islands. J Mater Chem 2011;21:11854–61.
- [5] Choi W, Termin A, Hoffmann MR. The role of metal ion dopants in quantum-sized TiO<sub>2</sub>: correlation between photoreactivity and charge carrier recombination dynamics. J Phys Chem 1994;98:13669–79.
- [6] Zhang L, Yu JC. A simple approach to reactivate silver-coated titanium dioxide photocatalyst. Catal Commun 2005;6:684–7.
- [7] Pelaez M, Nolan NT, Pillai S, Seery MK, Falaras P, Kontos AG, et al. A review on the visible light active titanium dioxide photocatalysts for environmental application. Appl Catal B 2012;125:331–49.
- [8] Holman JP. Heat Transfer. 2<sup>nd</sup> ed. New York: McGraw-Hill; 1990.
- [9] Büettner J, Gutiérrez M, Henglein A. Sonolysis of water-methanol mixtures. J Phys Chem 1991;95:1528-30.
- [10] Kohno M, Mokudai T, Ozawa T, Niwano Y. Free radical formation from sonolysis of water in the presence of different gases. J Clin Biochem Nutr 2011;49:96–101.
- [11] Butler MA, Abramovich M, Decker F, Juliao JF. Subband gap response of  $TiO_2$  and  $SrTiO_3$  photoelectrodes. J Electrochem Soc 1981;128:200–4.
- [12] Onda K, Li B, Petek H. Two-photon photoemission spectroscopy of  $TiO_2(110)$  surfaces modified by defects and  $O_2$  or  $H_2O$  adsorbates. Phys Rev B 2004;70:045415.
- [13] Pallotti DK, Orabona E, Amoruso S, Aruta C, Bruzzese R, Chiarella F, et al. Multi-band photoluminescence in TiO<sub>2</sub> nanoparticles-assembled films produced by femtosecond pulsed laser deposition. J Appl Phys 2013;114:043503.

- [14] Linic S, Christopher P, Ingram DB. Plasmonic-metal nanostructures for efficient conversion of solar to chemical energy. Nat Mat 2011;10:911–21.
- [15] Beck JJ, Polman A, Catchpole KR. Tunable light trapping for solar cells using localized surface plasmons. J Appl Phys 2009;105:114310.
- [16] Zhang X, Chen YL, Liu R-S, Tsai DP. Plasmonic photocatalysis. Rep Prog Phys 2013;76:046401.
- [17] Tominaga J. The application of silver oxide thin films to plasmon photonic devices. J Phys Condens Matter 2003;15:R1101.
- [18] Allen JP, Scanlon DO, Watson GW. Electronic structures of silver oxides. Phys Rev B 2011;84:115141.
- [19] Tanaka A, Hashimoto K, Ohtani B, Kominami H. Non-linear photocatalytic reaction induced by visible-light surface-

plasmon resonance absorption of gold nanoparticles loaded on titania particles. Chem Commun 2013;49:3419–21.

- [20] Museur L, Kanaev A. Near band-gap photoluminescence properties of hexagonal boron nitride. J Appl Phys 2008;103:103520.
- [21] Le THH, Mawatari K, Kitamura K, Yatsui T, Kawazoe T, Ohtsu M, et al. In: The proceedings of the 14th International Conference on Miniaturized Systems for Chemistry and life science (μTAs2010),Groningen, The Netherlands; 2010. p. 1889–991. http://www.rsc.org/binaries/LOC/2010/PDFs/ Papers/643\_0258.pdf.
- [22] Le THH, Mawatari K, Pihosh Y, Kawazoe T, Yatsui T, Ohtsu M, et al. Optical near-field induced visible response photoelectrochemical water splitting on nanorod TiO<sub>2</sub>. Appl Phys Lett 2011;99:213105.