

## Synthesis and characterization of Ag/TiO<sub>2</sub> plasmonic photocatalyst supported on stainless steel webnet

Mojtaba Khani<sup>1</sup>, Nor Aishah Saidina Amin<sup>1\*</sup>, Zaki Yamani Zakaria<sup>1</sup>, Hajar Alias<sup>1</sup>, Seyed Nezamedin Hosseini<sup>2</sup>

<sup>1</sup> Chemical Reaction Engineering Group (CREG)/Low Carbon Energy Group, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor Baharu, Johor, Malaysia.

<sup>2</sup> Research and Production Complex, Pasteur Institute of Iran (IPI), Tehran, Iran.

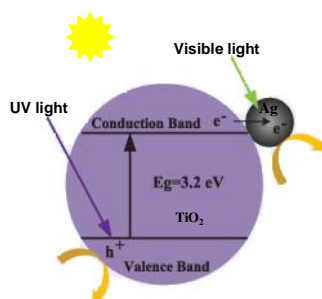
\*Corresponding Author: norainshah@cheme.utm.my

### Article history :

Received 25 October 2015

Accepted 15 November 2015

### GRAPHICAL ABSTRACT



### ABSTRACT

Plasmonic nanostructures present substantial function in the advancement of modern materials science and technology. Plasmon-enhanced solar light is harvested to enhance the solar-to-fuel energy conversion efficiency. Both organic and inorganic semiconductor materials often serve as photocatalysts for the direct conversion of solar energy into fuels, owing to their superior stability, environmental compatibility and photocatalytic activity. However, semiconductor efficiency can be hindered by their inability to absorb visible light due to the vast band gap. More recently, a number of research has been performed to enhance photocatalyst and photovoltaic device efficiency by integrating plasmonic nanoparticles (NPs) with semiconductor materials. The presence of plasmonic NPs causes greater semiconductor absorption cross sections due to robust field enhancement, light absorption at longer wavelengths and enhanced electron-hole charge separation in semiconductor media, thus maximizing the efficiency of photocatalytic devices. In this study, we have prepared a new visible-light-driven Ag/TiO<sub>2</sub> nanoparticles plasmonic photocatalyst coated on webnet stainless steel by the dip-coating method to enhance the visible light plasmonic photocatalyst. FESEM, EDX and UV-vis spectra analyses were carried-out to characterize the prepared catalysts. According to these tests, the Ag/TiO<sub>2</sub> coated on the stainless steel webnet functioned quite well. In addition, the maximum conversion of carbon dioxide was achieved at about 20%. This study may provide new insight into the design and preparation of advanced visible-light photocatalytic materials.

**Keywords:** plasmonic photocatalyst, Ag/TiO<sub>2</sub>, webnet

© 2015 Penerbit UTM Press. All rights reserved  
<http://dx.doi.org/10.11113/mjfas.v11n3.383>

## 1. INTRODUCTION

Currently, harvesting solar light as efficiently as possible is a very challenging problem that is intensively being investigated by numerous researchers globally. The aim is to meet the world's future energy requirements. As a copious and easily obtainable natural energy resource, sunlight has great potential in propelling environmentally friendly photochemical transformations [1]. The direct conversion of light energy into chemical energy or electricity by employing photocatalysts or photoactive materials has been of high interest recently. Despite momentous advancements attained in efficient material development for superior photocatalysis, the required efficiency for device commercialization remains a far prospect. The photocatalysts most often reported in the literature are based on semiconductor metal oxides [2]. Upon photon irradiation with energy exceeding the semiconductor band gap, charge separation takes place due to the electron transfer to the conduction band as well as holes remaining in the valence band. The separated charges (electrons and holes) migrate to the semiconductors

surface, catalyzing the chemical changes. Semiconductor nanoparticles display several exceptional properties compared to their bulk counterparts. In terms of electronic properties, semiconductor nanoparticles can be tuned easily by adjusting their chemical composition and dimensions. Semiconductor nanomaterials additionally have advantages including elevated physical and chemical stability as well as low cost. A range of semiconductor material types have been applied as photocatalysts in water treatment, water splitting and solar energy conversion [3, 4]. Nonetheless, semiconductor efficiency is restricted for the following reasons. (I) Inability to utilize visible light: the majority of popular semiconductors absorb only UV light on account of their large band gap, accounting for roughly 4% of total solar radiation and around 50% of visible light [5]. For instance, the TiO<sub>2</sub> band gap is roughly 3.2 eV, and so it displays photocatalytic activity only under UV light excitation. (II) Rapid photo-generated electron-hole pair recombination: electrons in the conduction band can recombine rapidly with valence band holes prior to migrating to the surface [6]. Therefore, in enhancing semiconductors' photocatalytic efficiency, various

strategies have been implemented. One method includes non-metal atom doping to narrow the band gap in conjunction with organic dyes to expand light absorption to longer wavelengths. Another method entails integrating plasmonic metal nanoparticles to diminish recombination and harvest visible light. Joining plasmonic metal NPs with semiconductors is a very good way of improving the photocatalytic efficiency of semiconductors, owing to the plasmonic metals' distinctive optical and electric properties. Au and Ag NPs have been most broadly employed for plasmon-enhanced solar light harvesting. According to Fig. 1, metal NPs much smaller than the light wavelength generate coherent oscillation of the conduction band electrons due to the interaction with an electromagnetic field. This is known as localized surface plasmon resonance (LSPR) [7].

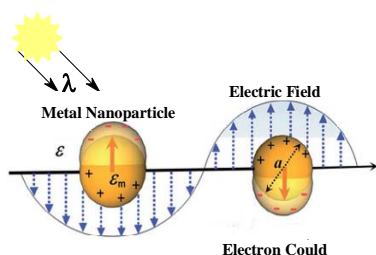


Fig. 1 Schematic representation showing the origin of surface plasmon resonance due to the coherent interaction between the electrons in the conduction band and light with wavelength  $\lambda$

Compared with traditional semiconductor photocatalysis, plasmonic photocatalysis has two distinct features: a Schottky junction and LSPR. Each feature benefits photocatalysis differently. For example, the Schottky junction results from the contact between metals and semiconductors. It is built on an internal electric field in a region (space charge region) in the photocatalyst, outside but close to the metal/semiconductor. This forces the electrons and holes to move in different directions when they are in or near the Schottky junction [8].

In the visible region, the LSPR absorption of Ag NPs can significantly increase the energy of trapped electrons through the strong local electron field of the LSPR effect, which causes them to be more easily transferred and react with electron acceptors. Nevertheless, SPR absorption of Ag NPs cannot effectively generate a photocatalytic reaction. The excitation–enhancement synergistic photocatalytic mechanism is displayed in Fig. 2. First, the  $\text{TiO}_2$  electrons are excited by UV light to the conduction band and are transferred to Ag NPs. Afterward, the trapped electrons' energy increases due to the SPR effect of Ag NPs. The synergistic effect is obtained between SPR enhancement and UV light excitation, which leads to the optimum photocatalytic performance of  $\text{CO}_2$  reduction on the  $\text{Ag}/\text{TiO}_2$  surface [9]. Immobilized  $\text{Ag}/\text{TiO}_2$

nanoparticles coated on webnet stainless steel was developed as a photocatalyst that can use visible light in high efficiency under sunlight irradiation in this study. The stainless steel webnet was selected as a photocatalyst support due to its large surface area that can provide more active sites for  $\text{TiO}_2$  deposition than general supports and because it facilitates the best ventilation for passing gases.

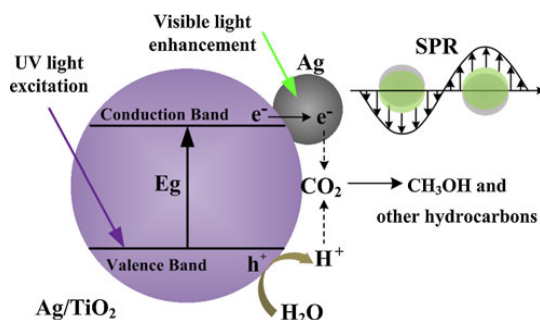


Fig. 2 The excitation–enhancement synergistic mechanism for the photocatalytic reduction of  $\text{CO}_2$  on  $\text{Ag}/\text{TiO}_2$  composite

## 2. EXPERIMENTS

### 2.1 Materials

Titanium dioxide P-25 (Anatase/Rutile: 80/20, particle size: 25 nm, surface area:  $55 \pm 15 \text{ m}^2/\text{g}$ ), silver nitrate were used to coat the stainless steel webnet with 60 mesh size that were supplied by Sigma company. Ethanol (99.8%), 2-Propanol (99.9%) nitric acid (65%), Sulfuric acid (30%) and acetone were obtained from Merck.

### 2.2 Catalyst Preparation

A simple and efficient method (dip coating) was applied in the current study for  $\text{Ag}/\text{TiO}_2$  nanoparticle immobilization [10]. The same technique with minor changes was applied to prepare  $\text{Ag}/\text{TiO}_2$  coatings onto stainless steel webnets to be used as photocatalysts. In coating the supports with titanium dioxide, titania slurry was first prepared as follows: initially, 10 g of  $\text{TiO}_2$  powder was added to 200 mL of AR grade ethanol as the base slurry medium, in which  $\text{TiO}_2$  powder can disperse adequately. The solution was stirred for 2 hr. Next, 5 mL of diluted nitric acid with pH 3.5 was added to the slurry. Suitable slurry acidity is necessary for the titania powder to disperse adequately. By adding the acid, the slurry became more uniform and the cloudiness began to disappear. This technique and with the same chemicals named has been employed earlier and often serves as a standard photocatalytic reactivity method [11]. Next, the slurry was sonicated for 30 min to separate the aggregated  $\text{TiO}_2$  powder and obtain more uniform slurry. Subsequently, 200 ml of 2-propanol was added to the solution and placed

under UV light. At this time under the UV light, about  $9.38 \times 10^{-5}$  (mole/liter) of  $\text{AgNO}_3$  was added given time to reduce the partial  $\text{Ag}^+$  ions in the  $\text{AgNO}_3$  particles to Ag species under irradiation. A fraction of the photoelectron population has reduced silver ions directly by the reaction shown in equation (1). The slurry color changed from white to yellow. A stainless steel webnet as a support was previously cleaned with sulfuric acid, acetone and distilled water and then immersed into the slurry. The webnet was dried in the oven for 1 hr at  $120^\circ\text{C}$ . In the final coating process stage, the catalyst was calcined in a furnace at  $450^\circ\text{C}$  for 30 min. The sample was then stored in a vacuum desiccator. Upon coating process completion, the catalyst was ready for use.



### 2.3. Catalyst Testing

For catalyst testing,  $\text{Ag}/\text{TiO}_2$ -doped steel mesh was placed in the reactor and covered with a gasket seal. The reaction with gas feed containing  $\text{CO}_2$  and  $\text{CH}_4$  was constantly exposed to the visible light emitted for 2 hr. The maximum conversion of carbon dioxide was achieved at about 20%.

## 3. RESULTS AND DISCUSSION

The morphology of the catalyst was investigated using FESEM. Fig. 3 presents typical FESEM images of the  $\text{Ag}/\text{TiO}_2$  photocatalyst prepared on No. 60 mesh as well as the  $\text{TiO}_2$  powder. The morphologies of the  $\text{Ag}/\text{TiO}_2$  photocatalyst and neat  $\text{TiO}_2$  are displayed in Figs. 3.b and 3.c, respectively, outer diameters of these Ag nanoparticles are between 30-40 nm and the surface morphology of the stainless steel webnet No. 60 mesh coated with  $\text{Ag}/\text{TiO}_2$  prior to the photocatalytic reaction is shown in Fig. 3.a. For the webnet coated with titania particles, the FESEM observation indicated that the coating and webnet bonded well. Surface morphology is crucial in photocatalytic activity. Before the photocatalytic reaction, the photocatalyst surface must absorb the reactants. Consequently, the photo-generated electrons and holes move from the inside toward the surface, after which photodecomposition occurs. The uniform calcined photocatalyst surfaces may boost light absorption, but it is easy for  $\text{TiO}_2$  to agglomerate. The uniform calcinated photocatalyst structure is illustrated in Fig. 3.b as a FESEM image.

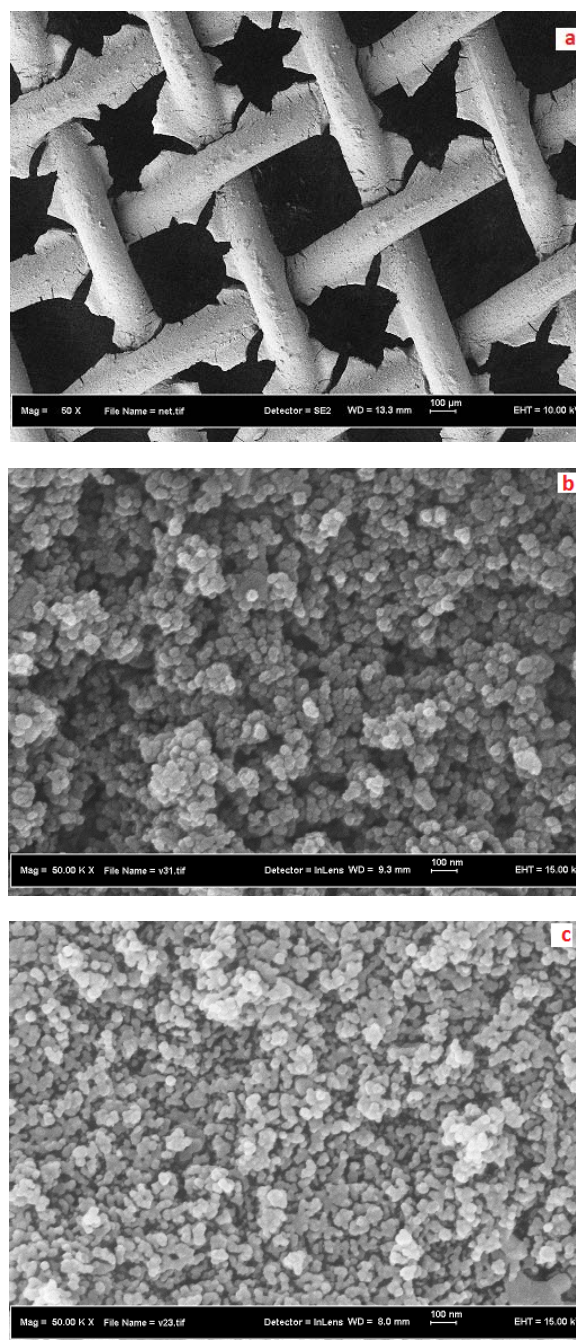


Fig. 3 FESEM images for a)  $\text{Ag}/\text{TiO}_2$  on the mesh size 60, b)  $\text{Ag}/\text{TiO}_2$  powder, c)  $\text{TiO}_2$  powder

Besides secondary electron imaging, backscattered electron imaging and Energy Dispersive X-ray (EDX) analysis are useful, extensively employed tools for chemical analysis. The intensity of backscattered electrons produced by electron bombardment is associated with the atomic number of elements in the sampling volume, thus revealing qualitative elemental information. The specific X-rays produced from the sample act as fingerprints,



providing sample elemental data, such as semi-quantitative analysis, quantitative analysis, line profiling and spatial distribution of elements. Fig. 4 presents the EDX results for the Ag/TiO<sub>2</sub> plasmonic photocatalyst. In spectrum peaks associated with Ti, O and Ag are observed. Ti and O peaks result from TiO<sub>2</sub> NPs. Quantitative analysis of these spectra gives the deposited materials a possible composition of Ag/TiO<sub>2</sub>, which agrees with the fact that these NPs were formed during Ag/TiO<sub>2</sub> deposition experiment. The EDX analysis of 0.2 wt.% Ag/TiO<sub>2</sub> NPs and confirmed the presence of Ag-metal in TiO<sub>2</sub> NPs.

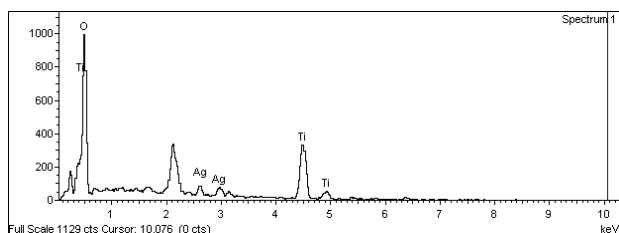


Fig. 4 EDX spectra of Ag/TiO<sub>2</sub>

UV-vis light absorption is a significant factor for the advancement of photocatalyst properties. Fig. 5 represents a comparison of the UV-vis absorption spectra of the Ag/TiO<sub>2</sub> photocatalyst and neat TiO<sub>2</sub> powder at room temperature. It is evident that Ag/TiO<sub>2</sub> NPs photocatalyst prepared had a broad absorption band from the ultraviolet to the visible regions, and the maximum absorption peak identified was at 360 nm. The fine UV-vis light absorption performance using the prepared Ag/TiO<sub>2</sub> NP photocatalyst can be ascribed to its uniform microstructure.

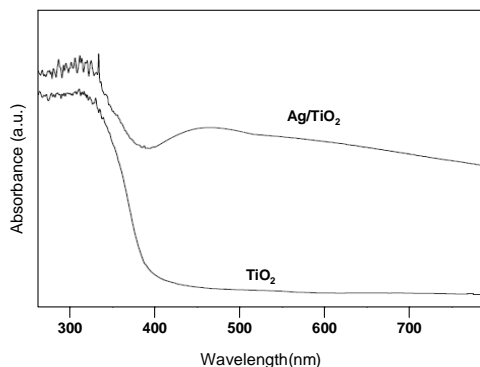


Fig. 5 The UV-vis absorption spectra of the Ag/TiO<sub>2</sub> NPs photocatalyst and commercial TiO<sub>2</sub>

#### 4. CONCLUSION

Noble-metal NPs are capable of absorbing visible light owing to the SPR phenomenon they undergo. When such NPs are to be employed as visible-light plasmonic photocatalysts, they should be deposited upon supports like

polar semiconductors or insulating oxides. When deposited upon an insulating oxide, no electron transfer takes place between the insulator support and the photoexcited NPs; therefore, the former does not directly participate in the photocatalysis process. On the other hand, in case of noble-metal NPs deposited onto a polar semiconductor, the semiconductor support is able to participate directly in the photocatalysis process because electron transfer occurs between the semiconductor support and the photoexcited NPs. A new visible light-driven plasmonic photocatalyst, *i.e.* Ag/TiO<sub>2</sub> NPs, was prepared by depositing Ag NPs onto TiO<sub>2</sub> NPs and subsequently reducing partial Ag<sup>+</sup> ions of the AgNO<sub>3</sub> particles to Ag<sup>0</sup> species under UV lamp irradiation, which is proposed on the basis of the fact that the Ag NPs are photoexcited due to plasmon resonance and charge separation, is accomplished by the transfer of photoexcited electrons from the Ag NPs to the TiO<sub>2</sub> conduction. Therefore, it is reasonably expected for plasmonic photocatalysis to play an even more significant role in air cleaning, environmental remedy, CO<sub>2</sub> reduction, water splitting and several other vital applications for human life. The integration of plasmonic nanostructures with semiconductors is a powerful strategy to exploit visible light-driven photocatalysts for solar energy conversion.

#### ACKNOWLEDGEMENTS

The authors would like to extend their gratitude to the Ministry of Education (MOE) and Universiti Teknologi Malaysia for the financial supports of this research under NanoMITE LRGS (Long Term Research Grant Scheme, Vot 4L839), RUG (Research University Grant, Vot 02G14) and FRGS (Fundamental Research Grant Scheme) (Vot 4F404).

#### REFERENCES

- [1] X. Lang, X. Chen, J. Zhao, Chem. Soc. Rev. 43 (2014) 473.
- [2] A. Primo, T. Marinto, A. Corma, R. Molinari, H. Garcia, J. Am. Chem. Soc. 133 (2011) 6930.
- [3] Y. Liu, J.R. Jennings, S.M. Zakeeruddin, M. Grätzel, Q. Wang, J. Am. Chem. Soc. 135 (2013) 3939.
- [4] A. Fujishima, K. Honda, Nature 238 (1972) 37.
- [5] G.L. He, M.J. Chen, Y.Q. Liu, X. Liu, Y.J. Liu, Y.H. Xu, App. Surf. Sci. 351 (2015) 474.
- [6] N. Zhou, V.L. Puente, Q. Wang, L. Polavarapu, I.P. Santos, Q.H. Xu, RSC Adv. 5 (2015) 290765.
- [7] X. Zhang, Y.L. Chen, R.S. Liu, D.P. Tsai, Rep. Prog. Phys. 76 (2013) 046401.
- [8] Z. Wang, J. Liu, W. Chen, Dalton T. 41 (2012) 4866.
- [9] E. Liu, L. Kang, F. Wu, T. Sun, X. Hu, Y. Yang, H. Liu, J. Fan, Plasmon. 9 (2014) 61.
- [10] A.S.E. Kalliny, S.F. Ahmed, L.C. Rietveld, P.W. Appel, Drink W. Eng. Sci. 7 (2014) 41.
- [11] M.T. Merajina, S. Sharifnia, S.N. Hosseini, N. Yazdanpour, J. Taiwan Inst. Chem. E. 44 (2013) 239.