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Research Article

The Photocatalytic Activity of SiO_2-TiO_2/Graphite and Its Composite with Silver and Silver Oxide

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Abstract

This research study the mixed semiconductor of SiO_2-TiO_2 which was immobilized on graphite substrate and also studies the effect of surface modification on its mixed semiconductor. The surface modification was carried out by electrode position of Ag from 0.4 M of $AgNO_3$ solution at various applied current. The electrode position was conducted for 30 minutes at 0.004; 0.008; 0.010; 0.012 and 0.014 A. In the electrode position cell, SiO_2-TiO_2/Graphite was used as cathode and a graphite rod was used as anode. The weight of deposited Ag was analyzed gravimetrically. The current efficiency of electrode position was calculated by comparing its experimental weight to its theoretical weight founded from calculation using Faraday's equation for electrolytic cell. Meanwhile, the photo electrochemical testing was carried out to investigate the efficiency of induced photon to current conversion; it was measured as %IPCE (% Induced Photon to Current Efficiency). The crystallinity and crystal structure of the prepared materials were analyzed by X-ray diffraction and their surface morphology was analyzed by Scanning Electron Microscope (SEM). This research found that silver was deposited as silver metal, Ag and as silver oxide, AgO. The electrode position efficiency at applied current of 0.014 A is 92.30 % with diameter of cluster is 7 - 11.9 mm. It is founded that Ag and AgO deposition enhanced the efficiency of photon conversion into current up to 89.92 %. The optimum %IPCE value is at 28.6 % of Ag content. Ag-SiO_2-TiO_2/G has higher photo conversion than Ag-TiO_2/G, shown by the %IPCE value at 300 nm is 83.25 % higher than Ag-TiO_2/G. It indicates the significant role of silica network in photo excitation mechanisms in the composite material.

Keywords: Ag; photocatalyst; semiconductor; SiO_2-TiO_2; surface modification

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1. Introduction

Semiconductor plays significant roles in human life due to it becomes a promising technology for environmental remediation such as for air and water purification, wastewater treatment and also as material for generating energy such as for solar cell and for battery [1]. Those important roles inspire some researchers to conduct researches on semiconductor materials in order to increase their performance. Mixed photo to catalyst has been studied by some researchers [2-4] due to those mixed photo catalyst perform better charge separation than single semiconductor and therefore suppress electron-hole recombination resulting better photo catalytic performance. That semiconductor also might be engineered to be expanded their photoresponse

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especially into visible light area by mixing it with other material that has good photorespon in visible light, such as CdS or inorganic complex that can serve as sensitizer. Linsebigler *et al*. [5] synthesized a CdS-TiO_2 composite and found that the coupling semiconductor shows enhancement of photo catalytic efficiency through charge separation, i.e. hole-excited electron separation then each charge can move freely to the semiconductor surface and serve as oxidator or reductor. Xe and Yuan [6] doped Ce^{4+} into Titania sol and nanocrystalline Titania and found that Ce^{4+} doped-titania sol has higher photo catalytic efficiency than nanocrystallite Titania. Meanwhile, Nugraheni [7] prepared composite of TiO_2 with SiO_2 with Na_2SiO_3 was used as precursor for silica and $TiCl_4$ was used as precursor for TiO_2. A 16 mM cetyl trimethyl ammonium (CTAB) solution was used as mesopore template.

There are some methods for preparation of photo catalytic semiconductor that have been investigated by some researchers, such as spin coating method [8-9], magnetron sputtering [10], chemical bath deposition [11,12], chemical vapor deposition [13] and also dip coating method [14,15]. Immobilization of semiconductor on a substrate has been considered as an effort to reduce cost of post treatment, such as for separation of the photo catalyst powder from the degraded solution. Moreover, recovery and recycling process can be conducted easier for the immobilized form. Therefore, some researchers interest to conduct researches on the immobilized form of semiconductor, such as Zhou *et al*. [15] who have prepared SiO_2-TiO_2 composite on glassy ceramic substrate by dip coating method from tetrabutyl orthotitanate ($Ti(Obu)_4$) and tetraethyl orthosilicate (TEOS) as precursors. Meanwhile, Whang *et al*. [14] prepared a thin film of SiO_2-TiO_2-PDMS composite by dip coating method from TEOS and polydimethylsiloxane (PDMS) which were mixed with titanium isopropoxide (TiOPr) as precursors and used acid solution as catalyst. The sol-gel and hydrothermal method of synthesis have been considered as good alternative for SiO_2-TiO_2 preparation due to no requirement of high temperature. Sol-gel method for mesoporous silica-titania composite is also reported by Shao *et al*. [2] with TiOCl solution and sodium silicate as precursor in the absence of CTAB surfactant. Meanwhile, Nichi *et al*. [16] used sol-gel preparation of nanoscale TiO_2/SiO_2 composite and Huang *et al*. [17] also used sol-gel method on the synthesis of polyaniline-modified Fe_2O_3/SiO_2/TiO_2 composite. A sol-gel route also applied by Wang *et al*. [18] to prepare a polyimide/silica/titania nanohybrids. It was found by Wang and coworkers that introduction of SiO_2 detain the aggregation behavior of TiO_2 on polyimide matrix.

Metal deposition on semiconductor surface is a modification method of semiconductor in accordance to enhance photo catalytic activity of the semiconductor. The enhancement of photo catalytic activity as the result of metal surface modification has been recorded since 1980 by Sato and White [19] in photo catalytic conversion of H_2O into O_2 and H_2. Loganathan *et al*. [20] doped silver, gold and platinum into TiO_2 nanoparticle, and found that Au doped TiO_2 (0.5 wt%) has the highest photo catalytic activity due to cathodic influence of gold in suppressing the electron-hole recombination during the reaction. In our previous study, metal surface modification on TiO_2/Graphite by electrode position of Cu and Ag and found the enhancement of photo catalytic activity in disinfection on Escherichia coli-contaminated water [12]. Ag metal has high standard reduction potential, i.e. 0.799 Volt, it indicates low possibility to be oxidized and high possibility to receive electrons and become the electron trapper for the excited electrons, e^-, in conduction band, then it can increase separation between the excited electrons to the holes, h^+ and allows e^- and h^+ to move freely to surface and become oxidiser and reductor for the targeted molecules.

This paper discusses the investigation of the photo catalytic activity of TiO_2-SiO_2 on graphite substrate and its modification with Ag and AgO deposition. Investigates the effect of Ag and AgO on the photo catalytic activity. Then compare the results to the photocatalytic activity of TiO_2/Graphite and Ag-TiO_2/Graphite which were published previously, in order to determine the contribution of the presence of SiO_2. The photo catalytic activity has been determine through the measurement of % Induce Photon to Current Efficiency (%IPCE).

2. Materials and Methods

The chemicals were used in this research have pro analysis grade. Titanium (IV) chloride ($TiCl_4$) (Merck) was used as TiO_2 precursor, Sodium Silicate (Na_2SiO_3) (Merck) as precursor of silica, CTAB surfactant (Merck) for linking agent between silica-titania network to graphite substrate and also as pore template of composite, graphite rods (product of ABC battery industry, Indonesia) were sliced into thin tablets and being used as substrate after being cleaned with deionized - water and ethanol. An-

$AgNO_3$ (Merck) was used for preparing 0.4 M of $AgNO_3$ solution. Meanwhile, Kalium Iodide (Aldrich), I_2 (Merck) in acetonitryl solution were used as electrolyte and ion-pairing reagent in photo electrochemical test to measure the %IPCE value.

In preparation of SiO_2-TiO_2 mixture, 6.2 ml (which is similar to 0.070 mol) of Na_2SiO_3 was poured into 20 ml ethanol, then 2.7 ml of HCl 37 %, 3 ml of H_2O and a definite amount of CTAB 16 mM (the definite amount was based to calculation to get ration of mol of H_2O to Na_2SiO_3 is 2.385). In other vessel, 2.9 ml of $TiCl_4$ was dissolved in 10 ml of methanol and 10 ml of isobutanol was added to reduce the hydrolysis rate of $TiCl_4$.

The Na_2SiO_3 solution was being refluxed and $TiCl_4$ solution was added gradually under stirred condition at 70 °C. After all $TiCl_4$ was added into Na_2SiO_3 solution and the mixture has became homogeneous, then the reflux process was stopped and the mixture was sealed and stirred for 3 days until it became gel. A 4.12 ml of NH_4OH solution then being added to the gel followed by heating at 70 °C and stirred for 1 hour. Then it was added by 5.9 mL aquadest and it was heated at 120 °C for 1 day. The produced SiO_2-TiO_2 powder was then being calcined at 1100 °C [7].

The immobilized SiO_2-TiO_2 mixture was prepared by dip coating method, by dissolved 0.2 g of SiO_2-TiO_2 mixture in 25 ml methanol and then 2 graphite tablets with diameter of each 0.8 cm were dipped into these solution for 5 minutes and then dipped repeatedly with 5 minutes for each dipping during 18 hours. The immobilized SiO_2-TiO_2 mixture in graphite substrate then being cleaned by deionized- water and being heated at 110 °C for 4 hours [21].

Silver was deposited electrically from 0.4 M of $AgNO_3$ solution at various currents of 0.004; 0.006; 0.008; 0,010; 0.012 and 0.014 A. Electrode position process was carried out for 30 minutes in Analytic Analyzer Electrolysis Yanaco AES-2D.

Gravimetric analysis was carried out to measure the weight of silver deposited. Crystallinity and crystal structure of the prepared materials were analyzed by XRD (X-ray diffraction Shimadzu 6000) at 2θ of 20-80 °. Morphological analysis was conducted on the prepared materials by Scanning Electron Microscope (Analytical Scanning Electron Microscope Jeol JSM-6360LA). Meanwhile, the %IPCE was measured by using Deuterium lamp and Wolfram lamp (installed in UV Vis Spectrophotometer Seiki-Ogawa, the specification of the lamps are 100 mA and 10 mV). A solution of 0.1 M of Kalium Iodide and 0.1 M of Iodide solution in acetonitryle was used as electrolyte. A graphite rod was used as counter electrode. The current produce during light induction was recorded by a multimeter (Sanwa Multimeter Digital CD 751, scaling in mA, mV and W).

3. Results and Discussion

The synthesis of SiO_2-TiO_2 mixture through sol-gel method proceed in two steps, i.e. the hydrolysis, when the precursor reacts with water and followed by condensation process that changes the solution to become sol. After solvent vaporization, gel will be formed and after drying process the silica-titania mixture is formed. The diffraction pattern of silica-titania powder is described in Figure 1. The diffraction pattern in Figure 1 shows the characteristic peaks of the SiO_2-TiO_2, which are signed as ST. The ST peaks are dominated by some broaden peaks that indicates the amorphous phase. The mixture also contain rutile TiO_2 phase and there is no characteristic peaks of anatase. As high calcinations temperature, 1100 °C, might transform the anatase phase to rutile phase, as it was studied by Shao *et al*. [2] for a mesoporous silica-titania composite. The diffraction peaks of silica-titania, ST, present at 2θ of 23.95, 37.53, 45.31, 55.11, 62.32, 78.77, and

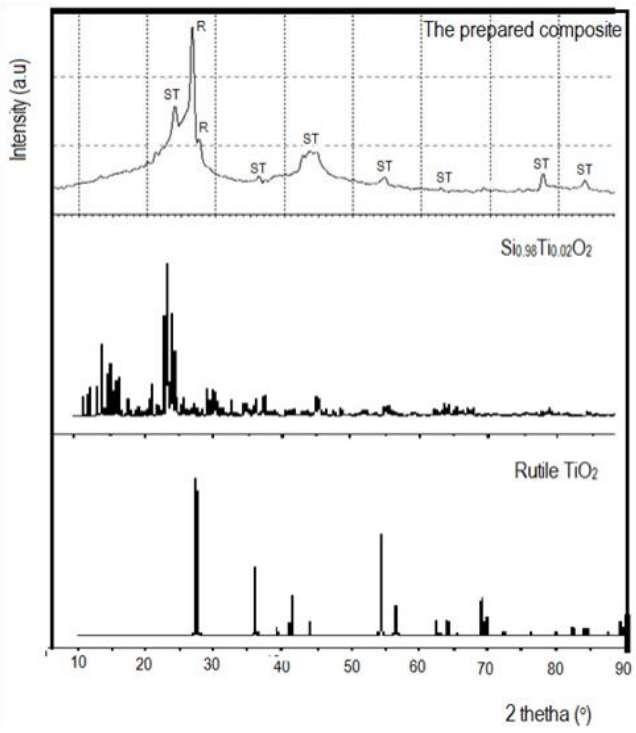

Figure 1. Diffraction patterns of TiO_2-SiO_2 mixture after being heated at 1100 °C. R refers to Rutile and ST refers to SiO_2-TiO_2 phase

84.55 ° as presented in standard diffraction of $Si_{2.98}Ti_{0.02}O_2$ ICSD#88413. Meanwhile, peaks at 2θ 25.45 and 26.52 ° refer to the characteristic peaks of rutile phase.

Electrodeposition of Ag from $AgNO_3$ solution at applied current of 0.004 A and 0.014 A produced composite material with diffraction patterns described in Figure 2. The diffraction patterns in Figure 2 shows the appearance of new peaks which are identified as Ag at 2θ 38.09 ° that matches to Ag standard diffraction ICSD#44387 with space group of FM3M, a face centered cubic structure and a peak at 2θ 45.37 ° is identified as Ag that matches to Ag standard diffraction ICSD#64707 with space group of P63/MMC, a primitive cubic structure. Some new peaks at 2θ 34.35, 37.35 and 56.85 ° which are identified as AgO based on the standard diffraction of AgO ICSD#27667. Morphological analysis by SEM also shows the present of Ag and AgO deposits as described in Figure 3. Ag and AgO clusters which were produced at 0.004 A of current have smaller size than that were produced by electrode position at 0.014 A, therefore the morphology of composite surface which were produced at 0.004 A is smoother, as it is described in Figure 3(b) and 3(c). The gravimetrical analysis to the prepared composites shows the different of composite weight as function of current, as listed in Table 1.

$$\%\ \text{current efficiency} = \frac{W_{\text{experiment ally}}}{W_{\text{theoretically}}} \times 100 \quad (1)$$

Meanwhile, the theoretical weight (Wtheo) was calculated based on Faradic equation for electrode position (Equation (2)).

$$W = \frac{Mr\ i\ t}{n\ F} \quad (2)$$

Mr is relative molecular mass (g.mol^{-1}), *I* is current (A), *t* is electrode position time (second), *n*

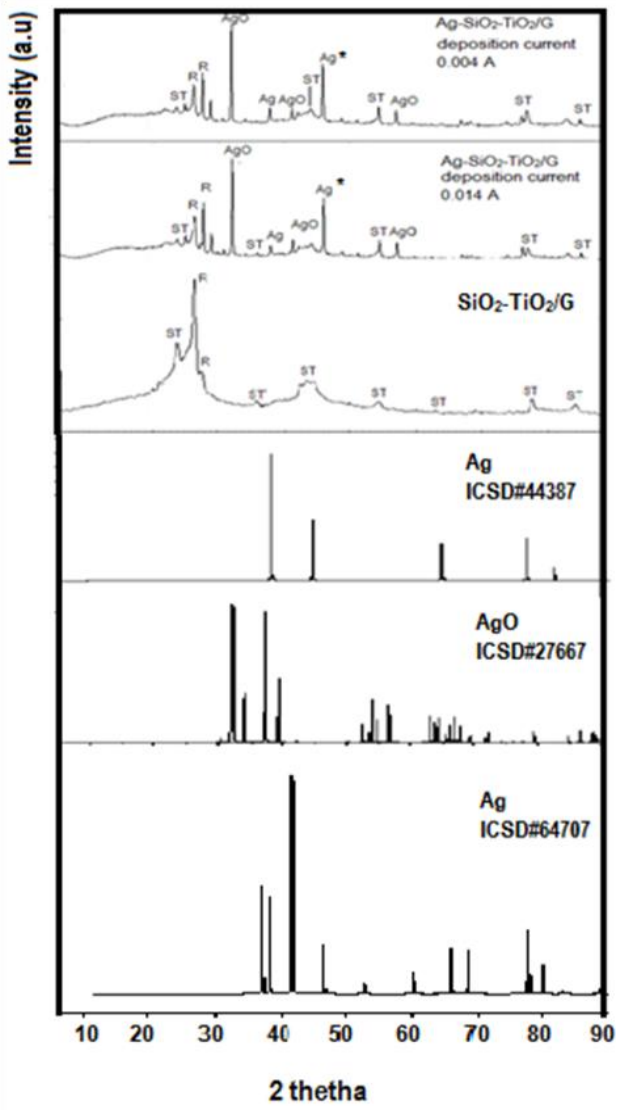

Figure 2. The diffraction patterns of Ag-TiO_2-SiO_2/Graphite, Ag was deposited at 0.004 A and 0.014 A of current. Ag* refers to characteristic peak of Ag corresponding to ICSD#64707

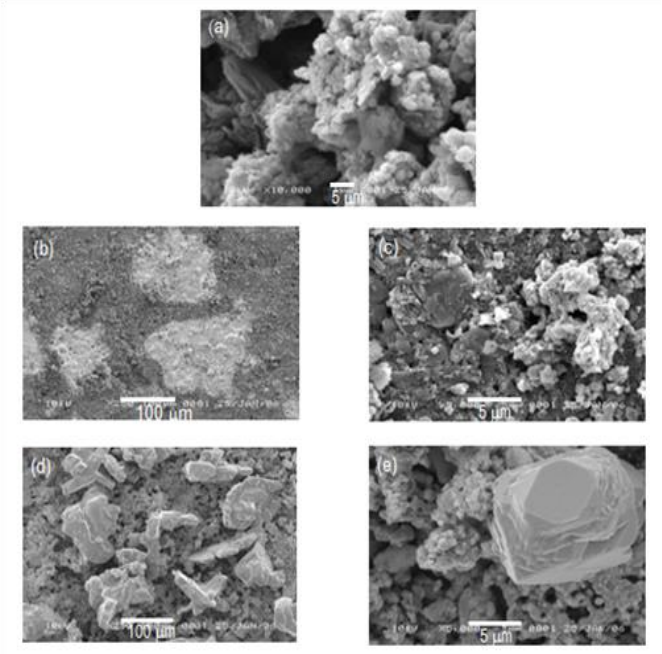

Figure 3. SEM images of (a) SiO_2-TiO_2/Graphite, (b) and (c) Ag-SiO_2-TiO_2/Graphite that prepared at 0.004 A of electrodeposition current, (d) and (e) Ag-SiO_2-TiO_2/Graphite that prepared at 0.014 A of deposition current.

is number of electrons contribute to the reaction (equation (3) and (4)) and *F* is the Faradic number (96500 C).

$$H_2O_{(aq)} \rightarrow \frac{1}{2} O_{2(g)} + 2 H^+_{(aq)} + 2e^- \qquad E^o_A = 1.23 \text{ Volt} \qquad (3)$$

$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)} \qquad E^o_C = 0.799 \text{ Volt} \qquad (4)$$

Gravimetrical analysis data in Table 1 shows that the higher the current was applied in electrodeposition process, the current efficiency decreases, except at 0.014 A. These probably due to some deposited silver fall out and the experimental weight then become non linear function to the applied current as it is stated in Faradic equation (Equation (2)). At applied current of 0.014 A, the current efficiency is high, i.e. 92.30 %. This probably due to different morphological characteristic of deposited Ag at 0.014 A. SEM images (Figure (3)) shows that the deposited Ag at 0.014 A has more regularly form, which is similar to cubic form with short side 7 mm and long side of 11.9 mm. Meanwhile, Ag and AgO which were deposited at current less than 0.014 A has irregularly form and smaller size. Those irregularly deposition may cause the connection between metal deposited and SiO_2-TiO_2 surface is weak and unstable.

Photo electrochemical testing on the prepared materials measured the %IPCE value that represents the conversion efficiency of induced photon to current at various wavelength of light (200 - 700 nm) (Figure 4). Those %IPCE represents the photo catalytic activity of each material due to the electrons that passed the external circuit and were detected by amperemeter were electrons that were excited by photon from valence band to conduction band then flowed to the current collector and measured by amperemeter.

Figure 4 shows that deposition of Ag and AgO on SiO_2-TiO_2/Graphite enhances the %IPCE value up to 89.92 % at ultraviolet wavelength, 300 nm and enhances the %IPCE value up to 84.06 % at visible light (500 nm). These prove that Ag and AgO could serve as electron trapper then reduce the possibility of electron-hole recombination. Schemes of the proposed mechanisms in SiO_2-TiO_2/G and Ag-SiO_2-TiO_2/G are depicted in Figure 5. Meanwhile, the relation between weights of metal deposited with the conversion efficiency of induced photon to current (%IPCE) at 300 nm is described in Figure 6. Polynomial trend line application to those %IPCE data found that the optimum silver content will be 28.6 %. Meanwhile, the comparison between %IPCE of Ag-SiO_2-TiO_2/Graphite, the material that is discussed in this paper with Ag-TiO_2/Graphite, the material which was published in our previous paper [12]

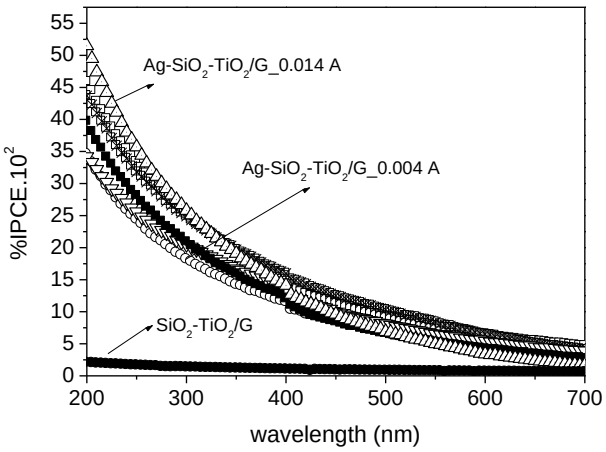

Figure 4. % IPCE of the prepared materials at 200 - 700 nm

Table 1. Weight of deposited silver as function of applied current and its calculated current efficiency (%) based on calculation using Equation (1)

Current (A)	Weight of deposited metal (g)		Current efficiency (%)
	Experimental weight	Theoretical weight	
0.004	$8.000.10^{-3} \pm 8.165.10^{-4}$	$8.048.10^{-3}$	99.404
0.006	$11.250.10^{-3} \pm 9.574.10^{-4}$	$12.072.10^{-3}$	93.191
0.008	$14.750.10^{-3} \pm 1.708.10^{-3}$	$16.096.10^{-3}$	91.638
0.010	$10.000.10^{-3} \pm 1.826.10^{-3}$	$20.120.10^{-3}$	49.702
0.012	$10.250.10^{-3} \pm 9.574.10^{-4}$	$24.145.10^{-3}$	42.452
0.014	$26.000.10^{-3} \pm 9.574.10^{-4}$	$28.169.10^{-3}$	92.300

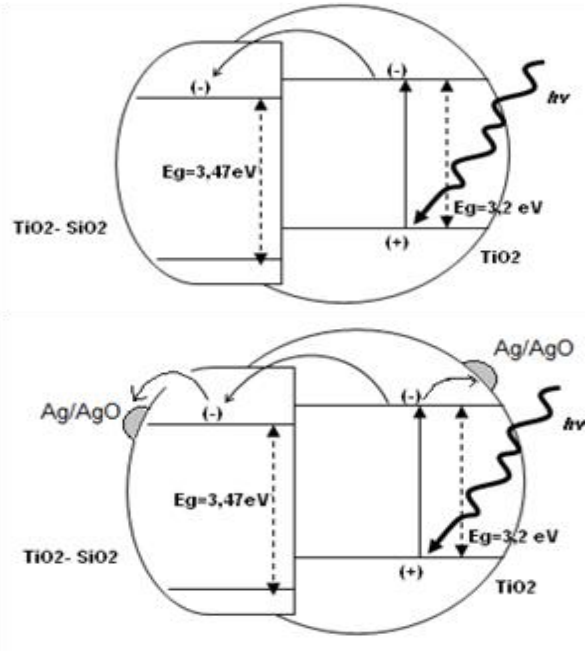

Figure 5. Schemes of the proposed photoexcitation mechanisms in TiO_2-SiO_2/G and Ag-TiO_2-SiO_2/G composite

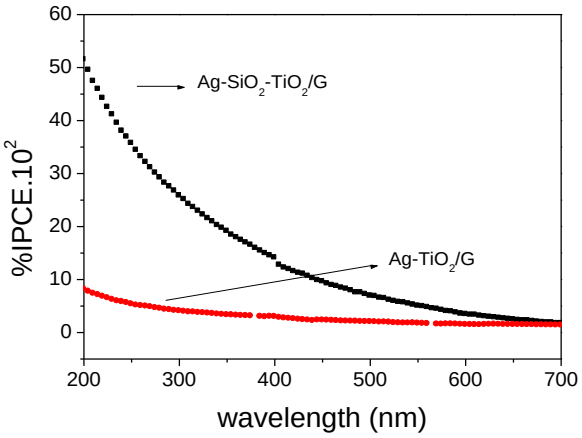

Figure 7. Comparison of %IPCE of Ag-TiO_2/Graphite and Ag-SiO_2-TiO_2/G. Ag was deposited at 0.014 A for 30 minutes

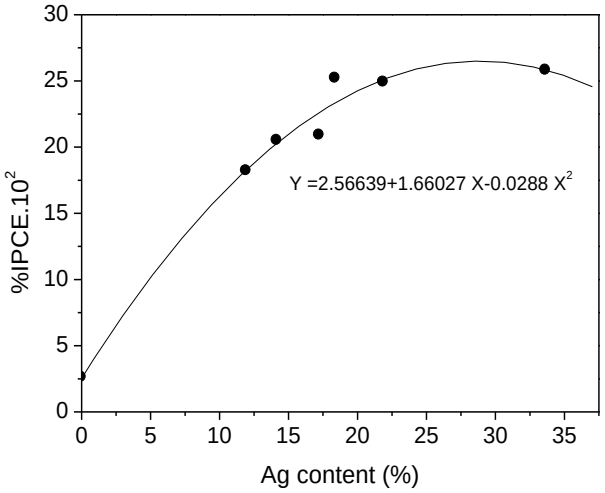

Figure 6. Curve of %IPCE at 300 nm of induce photon as function of Ag content (%)

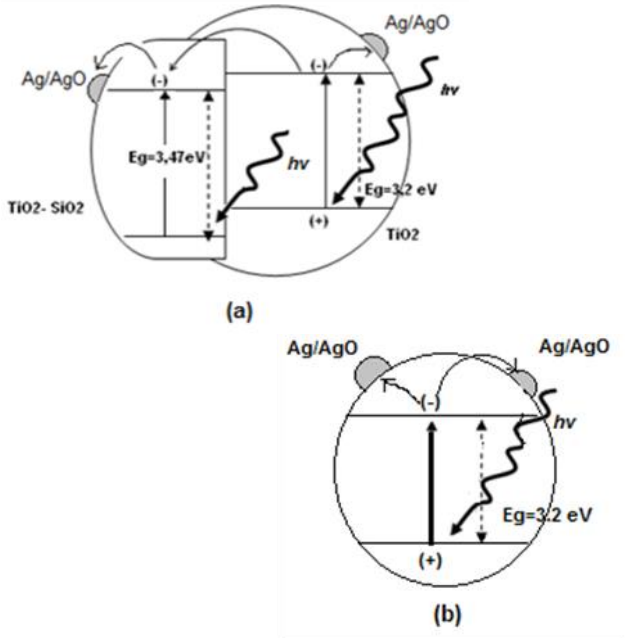

Figure 8. Scheme of photo excitation mechanism in (a) Ag-SiO_2-TiO_2/G, and (b) Ag-TiO_2/G

is plotted in Figure 7.

Figure 7 shows that Ag-SiO_2-TiO_2/G has higher %IPCE than Ag-TiO_2/G. It indicates that SiO_2 plays significant role in photo excitation mechanism. At induce photon of wavelength lower than 350 nm (comparable to more than 3.47 eV as the gap energy of SiO_2) the electrons in valence band of SiO_2 also can be excited to conduction band and contribute to the photo activity of this Ag-SiO_2-TiO_2/Graphite. The existence of Ag and AgO at SiO_2 surface can serve as electron trapper then flows those electrons to the external circuit. Moreover, SiO_2 itself also can serve as electron trapper for the excited electron from valence band of TiO_2 and this mechanism can reduce the possibility of electron-hole recombination. Hu *et al*. [22] who prepared the mixture of SiO_2/TiO_2 and TiO_2 core in SiO_2 shell (SiO_2-TiO_2) found that the recombination rate is decreased by the existence of SiO_2. This explanation was based on photo luminescence, PL, spectrum. PL emissions is the result of the recombination of the excited electrons with holes, therefore the lower the PL intensity indicates the decrease in recombination rate [22]. Mean-

while, in Ag-TiO_2/Graphite, only electrons of TiO_2 that contributes to photo excitation and also only Ag and AgO that can serve as electron trapper. Therefore, the photo catalytic activity, as it is refered by %IPCE value is lower than Ag-SiO_2-TiO_2/G. The proposed schemes for photo excitation mechanism in Ag-SiO_2-TiO_2/G and Ag-TiO_2/G are described in Figure 8.

4. Conclusions

Surface metal electrodeposition on SiO_2-TiO_2/Graphite produced deposited of Ag and AgO. The highest current efficiency of electrodeposition is at 0.004 A of applied current, i.e. 99.404 %. The results show that Ag and AgO deposition on TiO_2-SiO_2/Graphite composite significantly enhance the photocatalytic activity up to 89.92 % under UV irradiatio and up to 84.06 % under visible light irradiation. The optimum %IPCE value can be reached when the Ag and AgO content is 28.6 %. The conversion efficiency of induced photon to current of Ag-SiO_2-TiO_2/G is higher than Ag-TiO_2/G. It indicates the existence of SiO_2 contribute significantly to the photo activity of material.

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