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Mixed Anatase/Rutile Phase of Ag Doped TiO_2 Film for Dye Degradation

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ABSTRACT

Mixed anatase/rutile Ag doped titanium dioxide (TiO_2) film successfully fabricated with two simple step. Firstly, Ag doped rutile phase TiO_2 was fabricated by hydrothermal method at low temperature of 150°C for 10 hours and followed by various duration of immersion in tayca 320 solution for anatase phase. The various duration of immersion was studied to investigate the optimum time immersion to decorate anatase phase on Ag doped rutile phased TiO_2 film in assisting photocatalytic activity. The prepared samples were analyzed for their crystalline structure, morphology, composition, and photocatalytic activity using various analytical techniques such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDX) and methylene blue (MB) degradation. It was observed that mixed phased of Ag doped TiO_2 film shows an excellent photocatalytic activity compared with the single phase. The optimum immersion time is 1 hour. The photodegradation of 1 hour immersion film was reached 100 percent degradation only for 90 minutes and increased up to 19% compared with no anatase phase film. It was proved that mixed phases has better degradation compared with single phase. The anatase phase helps to avoid recombination between electron and holes pair by capturing the electron and enhanced the photocatalytic activity since the anatase decorated on smooth surface of the rod which is no active area for photocatalytic activity.

Key words: Ag doped, anatase, methylene blue, photocatalytic, rutile, TiO_2

1. INTRODUCTION

Environmental pollution become a serious problem originating from toxic organic pollutants in waste water that can harm the living organism. Releasing the toxic organic pollutant into various water bodies could abolish a fresh water resource. Therefore, an effective waste water treatment is desirable to save our environment for future generations. Generally, the conventional treatment of waste water were by flocculation, chemical oxidation, biological process, coagulation, membrane filtration and advanced oxidation process (AOP) [1], [2]–[4].

TiO_2 is one of the promising semiconductor that shows a great ability in AOP treatment [5]. Titanium dioxide (TiO_2) has been investigate since discovered by Fujishima and Honda in 1971 for water splitting [6]. The increasing of environmental problem in society urge the researcher to optimized the ability of TiO_2 photocatalyst in environmental purification. Several advantages of TiO_2 are chemical stability, low cost, reusability and chemical inertness [7]–[9]. These advantages make TiO_2 a multifunctional material that can be used in various fields such as dye-sensitised solar cell (DSSC) [10], gas sensor [11], water splitting [12], hydrogen generation [13], and self-cleaning [14]. Among TiO_2 nanostructures, TiO_2 nanoflowers gives high surface area and high porosity [15]. Due to its high surface area, TiO_2 nanoflowers were used in application which it gives better response. Several drawbacks of TiO_2 that limit the photocatalytic property such as wide band gap. The band gap of anatase phase (3.2 eV) and rutile (3 eV) has a wide gap that electron must have to excite from valence band to conduction band [16]–[18]. In addition, TiO_2 also has high recombination between electron and hole pairs [19]. Mixed phase between anatase and rutile shows the

synergistic effect for enhanced photocatalytic activity. Several studies has been done into the development of the mix phases between rutile and anatase in charge separation between electron and holes pair [20]. These drawbacks also can be counter with the doping process with metal, non-metal and transition metal [21], [22]. The incorporation of nobel metal such as Au, Al and Ag into the parent lattice of TiO_2 may overcome the drawbacks of the photogenerated electron lifetime [23]. This metal will act as electron trapped that can give a longer lifetime to the electron that can react with the target contaminants [24]. This may due to the location of Ag Fermi level lower than TiO_2 conduction band [25]–[27]. Ag particle also has the ability to generate surface plasmon resonance (SPR) that can lower the band gap energy and subsequently enhance the photocatalytic activity of the film [28]. Ag exhibit a great ability in anti-bacterial effect which is a huge advantages for waste water treatment [29]. The synergistic effect of anatase/rutile heterojuction with Ag as electron trapper leads to excellent photocatalytic activity. Generally, many preparations have been reported in metal doped fabrication such as sol-gel spin coating [30], [31], solvothermal method [32], [33], electro-chemical synthesis [23] and reduction by using UV irradiation [34]. Though, the above-mentioned methods have several disadvantages of insufficient contact, low efficiency and consume a long period to prepare the sample.

From the previous study, most of the researcher mainly concentrated in synthesizing TiO_2 powders due to the higher photocatalytic activity than immobilized catalyst or film [35]. However, the disadvantages of post-separation between treated water and powder after the photocatalytic process can cause more serious problem to the aquatic life. Moreover, powder catalyst also has a limit in continues flow system [36]–[38]. Preparation of the catalyst on a film or immobilized catalyst may possible to overcome the stated problem.

In this project, mixed anatase/rutile phase of Ag doped TiO_2 film will be prepared using two simple step which is hydrothermal process and immersion in tayca 320. Hydrothermal technique could be a liquid-deposit method exploitation soft chemistry and provides a uniform thin film assisted with stable temperature and pressure. This film is expected to solve the stated problem and enhanced the photocatalytic activity. The administration of the experiment was done with tayca 320 for differential duration immersion of various hours shows the degradation level of the dye in waste water treatment increased compared by without the assisting of anatase phase. The fabricated TiO_2 were characterized by the exploitation of XRD, EDX, FESEM, and photodegradation of MB to investigate the morphology, elemental structural and efficiency of the film in photodegradation.

2. MATERIALS AND METHODS

2.1 Fabrication of mixed phases AR-Ag/TiO_2 film

Fluorine doped tin oxide (FTO) substrate was used in this experiments. The FTO glass was cut into 35 mm x 35 mm dimension. The substrate was cleaned using sonication method by using acetone, ethanol and deionized (DI) water with the volume ratios of (1:1:1) for 10 minutes followed by drying in ambient air. First stage of fabrication was by using hydrothermal method to fabricate rutile phase of Ag/TiO_2 film. 80 ml DI water was mixed with 80 ml of HCl. The solution was stirred for 5 minutes. The hot plate was set to 212°C. Then, put 0.0569 g of $AgNO_3$ and continued stirring for 30 minutes. The temperature was reduced to room temperature and 0.1 M of TBOT was dropped wisely into the solution. Stirred the solution until the solution is cleared. Put the FTO substrate with conducting FTO surface facing upward and pour the prepared solution into the Teflon made liner. Place the autoclave inside the oven at 150 °C for 10 hours. The autoclave was taken out from the oven and cooled down at room temperature. The prepared sample was rinse with DI water several time and dried at 100°C for 30 minutes. The second step was prepared for the addition of anatase phased. The immersion duration of rutile phase of Ag/TiO_2 film in tayca 320 was varied for 1 hour and 2 h ours. After immersion the sample was annealed at 450°C for 1 hours. R-Ag/TiO_2 denoted as rutile phase of Ag/TiO_2 film without anatase phase. AR1-Ag/TiO_2 denoted as mixed phases of anatase and rutile that immersed for 1 hour in tayca 320 while AR2-Ag/TiO_2 denoted as 2 hour immersion.

2.2 Characterization mixed phases AR-Ag/TiO_2 film samples

The successful fabricated mixed phases AR-Ag/TiO_2 film from the hydrothermal method and immersion method is characterized by using FESEM JEOL-7600F to study the surface morphologies and the elemental property of the samples. The XRD PANalytical X-Pert Powder was used to examine the structural property. The result shows the x-ray intensity versus 2θ. The range of the 2θ value was set from 20 to 80 degree. The efficiency of prepared sample was tested by using photodegradation of MB. The concentration of MB after treatment was examine by using UV-Vis spectroscopy.

2.3 Photocatalytic degradation of MB

Photocatalytic experiments was conducted to investigate the ability of AR-Ag/TiO_2 film in dye degradation. MB was used as a model of a waste water. 5 PPM concentration of MB with pH 12 was used in this study. The film was exposed with Xenon lamp (150 watt) to eliminate the unwanted impurity on top of the sample for 30 minutes. Then, the sample was

immersed in 100 ml of MB solution in dark condition for 30 minutes to promote adsorption-desorption of the sample. Then, the sample was irradiated with light for 120 minutes. The whole reactor was covered in a black box to refrain it from other source of light. Figure 1 shows the illustration of photocatalytic reactor for this study.

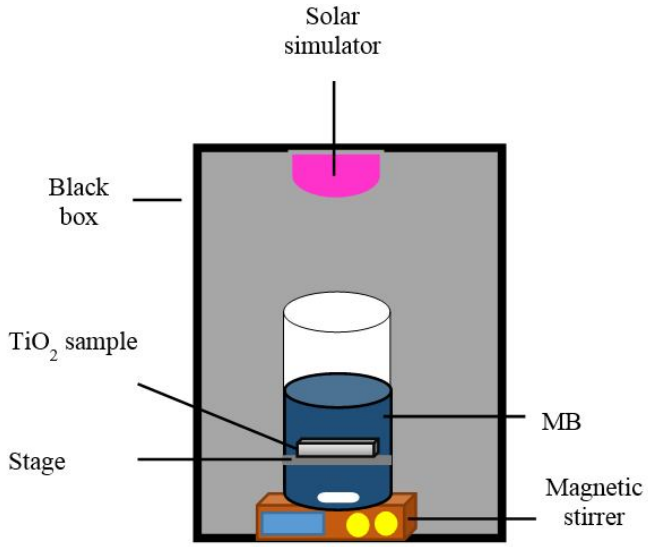

Figure 1: The illustration of photocatalytic reactor

At constant time interval, 3 ml of MB solution was withdrawn for sampling. The concentration of MB was observed at wavelength 664 nm. The percentage dye degradation was calculated by using Equation (1):

$$\text{MB degradation} = \frac{Ao - At}{Ao} \times 100 \quad (1)$$

Where A_o is the initial absorbance of MB solution and A_t is the absorbance of MB solution at time t.

3. RESULTS AND DISCUSSIONS

3.1 Structural property

The X-Ray Diffraction (XRD) characterization was used to study the structural properties of the TiO_2 samples. The XRD pattern shown in Figure 2 shows the TiO_2 were well crystalized. The peaks in XRD pattern shows anatase peak at 2 theta value of 25.28° on plane (101) and rutile peaks at 27.45°, 36.08°, 41.23°, 36.08° and are related to R(110), R(101), R(111) and R(211) planes [39]. No anatase peak was detected for R-Ag/TiO_2 sample. This may due to the acidic solution from the prepared sample that produce rutile phase. The acidic solution tend to produce rutile phase while alkaline solution tend to produce anatase phase in hydrothermal method [40]. The presence for anatase peak and rutile peaks can be viewed in the XRD spectra for both sample for AR1-Ag/TiO_2 and AR2-Ag/TiO_2. The anatase peaks was achieved by immersion with tayca 320 solution for each sample with time parameter of increment of 1 hour and 2 hours. Good crystallinity of catalyst will provide high electron mobility to the surface and enhanced the photocatalytic activity [41]. The role of anatase phase will explained in photodegradation of MB section. No Ag peak detected due to the lower percentage used and XRD unable to detect by XRD detector [27].

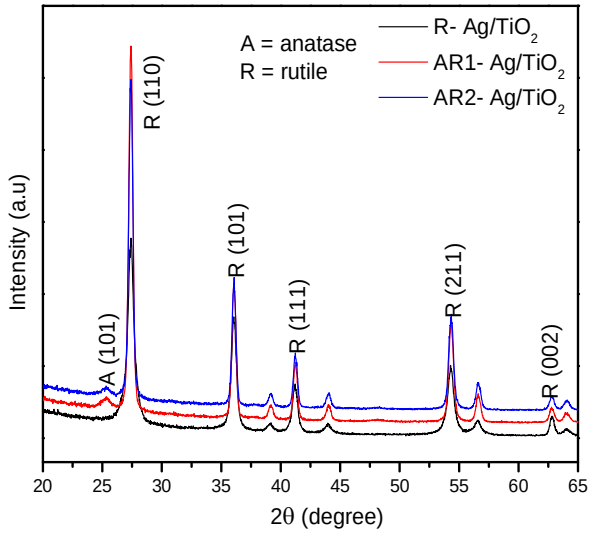

Figure 2: XRD pattern of R-Ag/TiO_2 film and AR-Ag/TiO_2 film prepared at 1 hour and 2 hours

3.2 Elemental analysis

Elemental analysis was conducted by using EDX to investigate the elemental property of the prepared sample. Figure 3 shows the area that chosen for analysis and the element that exist in the sample. All the sample has a titanium (Ti) and oxygen (O). No impurity detected on the sample proved that our sample has pure TiO_2 film. Table 1 shows the atomic percentage for prepared sample detected by EDX signal. The present of carbon (c) element may due to the carbon tape used during characterization of the sample. The R-Ag/TiO_2 sample shows Ti and O as 22.58% and 74.69 %, respectively. For AR1-Ag/TiO_2 sample shows Ti and O as 20.05 % and 76.62% while AR2-Ag/TiO_2 sample shows Ti and O as 23.46 % and 74.24 %. No significant different between the samples. The obtained atomic percentage for all sample which confirms the stoichiometry of TiO_2 elements.

Table 1: Atomic percentage of different sample

Element	R-Ag/TiO_2 (%)	AR1-Ag/TiO_2 (%)	AR2-Ag/TiO_2 (%)
Ti	**22.58**	**20.05**	**23.46**
O	**74.69**	**76.62**	**74.24**
C	**2.73**	**3.33**	**2.30**

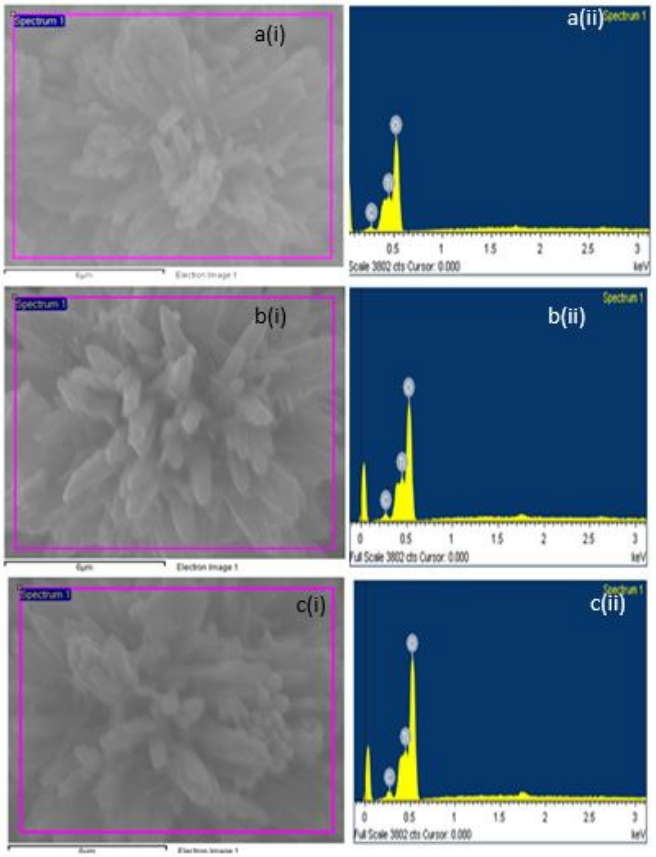

Figure 3: Elemental property of (a) R-Ag/TiO_2 film and AR-Ag/TiO_2 film prepared at (b) 1 hour and (c) 2 hours

3.3 Surface morphology

The field emission scanning electron microscopy (FESEM) is used to observe a surface morphology of the prepared sample. The FESEM has higher resolution, so that samples can be magnified at higher level. The surface morphology of the prepared TiO_2 film with different immersion hour duration are shown in Figure 4. It is indicated from figure 2(a) is without immersion while figure 4(b) has an hour of immersion and figure 4(c) has 2 hours immersion.

The rutile structure was formed from the chain of TiO_6 octahedral along the c-axis. The TiO_6 octahedral formed through one shared edge while two chain formed through points [42]. This may due to the Cl^- ions restricted hydrolysis of titanium and form the rods structure instead of particle [43]. Detail information about formation of flower-like structure was explained in detail elsewhere [44]. All the films shows a flowerlike structure. The size of the rod is range 90 to 120 nm. No changes on morphology was expected after the immersion process. There is a layer build up on the flowerlike structure as the rate of immersion increases. This may due to the tayca 320 is absorbed and attach on the flower of TiO_2. The annealing treatment after the immersion help the anatase nanoparticle to attach onto rods. The inset images in each images shows the tayca 320 was successfully attach on the flower TiO_2. The anatase nanoparticle with size 3-5 nm has decorated on the smooth surface of rods of flower and hence enhanced the active site for photocatalytic process to take place. The rod structure has an exhibit good electron mobility and efficient electron and hole separation over TiO_2 surface[45], [46]. In addition, flower-structure can produce multiple reflection that provide more photon for TiO_2 to generate electron [47].

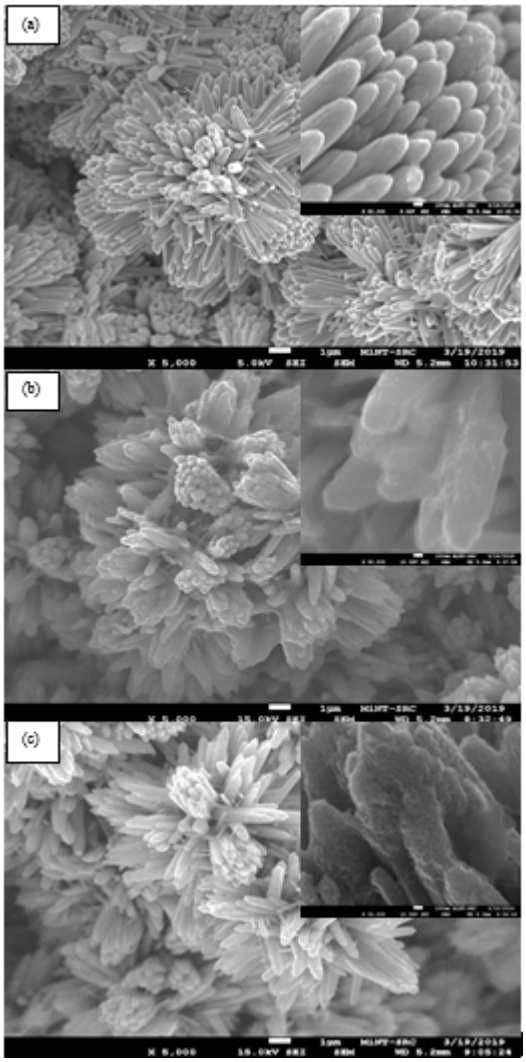

Figure 4: Surface morphology of (a) R-Ag/TiO_2 film and AR-Ag/TiO_2 film prepared at (b) 1 hour and (c) 2 hours

3.4 Photocatalytic analysis

The investigation of prepared sample towards MB degradation was conducted in order to find the efficiency. Figure 5 shows the decreasing initial absorbance of MB that disappeared almost completely after 90 minutes of irradiation at 664 nm wavelength. Figure 5(b) is the photolysis (absence of catalyst) experiment and was conducted to act as a reference. Figure 5(b)-(d) shows the absorbance result for R-Ag/TiO_2 and AR-Ag/TiO_2. The result also shows the time dependent of light irradiation of the prepared samples. Figure 6 shows degradation rate of MB is plotted against time to

observe the photocatalytic efficiency for all samples. The direct photolysis shows 66% degradation, R-Ag/TiO_2 film shows 85%, AR1-Ag/TiO_2 film has 98% and AR2-Ag/TiO_2 film has 94%. This results exhibits the anatase phase play an important role in enhancing photodegradation of MB. For R-Ag/TiO_2 film also has high degradation. It proved that the single crystalline which is rutile phase can provide good mobility. Then, Ag metal play an important role in capturing electron that act as electron trap. This phenomenon also agreed with previous study [48]. The Schottky barrier that develop between TiO_2 and Ag metal enhance the electron lifetime and provide more time for electron and hole to react with the targeted contaminants [49]. Moreover, the addition of anatase nanoparticle that developed from the immersion of tayca 302 give a huge advantage by providing active surface site. The anatase phase also assisted to hold electron more after being capture from R-Ag/TiO_2 film.

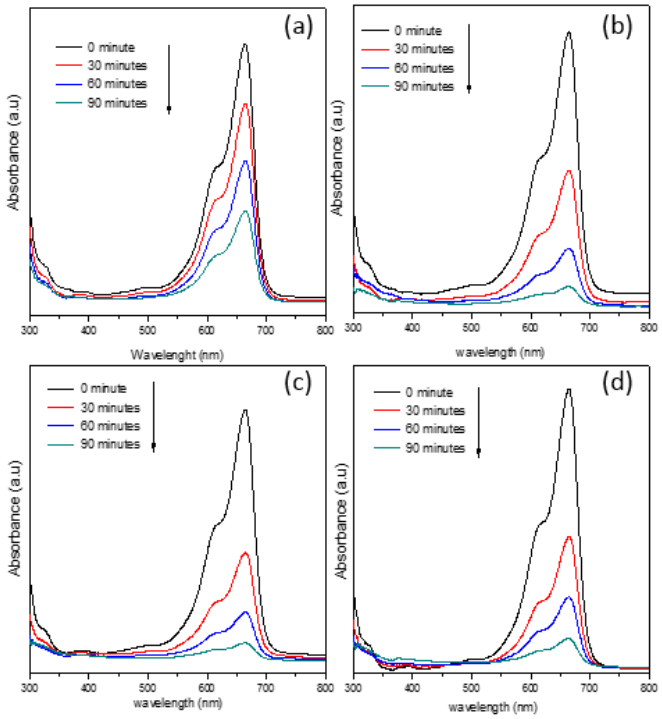

Figure 5: Photodegradation of MB for (a) photolysis (b) R-Ag/TiO_2 film and AR-Ag/TiO_2 film prepared at (c) 1 hour and (d) 2 hours

The 2 hours immersion shows the decreased in photodegradation which is only 94% degradation. This reduced result may be too much anatase nanoparticle decorated on the rods and act as the recombination centre. This phenomenon will lead to decrease the photocatalytic activity. In photocatalytic activity, several factors contribute to the high degradation such as crystallinity, surface morphology and surface chemistry [50], [51]. One of the important factor is lifetime electron that produce during the excitation. This will hold electron longer and help to electron and hole to react with the contaminants. Figure 7 shows the illustration of electron flow between anatase and rutile phase.

The electron excited from valence band (VB) to the conduction band (CB) upon irradiation that has enough energy. The photogenerated electron flow from anatase phase to rutile phase while the photogenerated hole flow from the opposite site from rutile phase to anatase phase. This may due to the anatase anatase/rutile heterojunction that exsist in bi layer film or composite powder [52], [53]. This heterojunction inhibit the recombination beween electron and hole. Subsequently, the electron was further trapped in Ag element and give more lifetime to the electron to react with the contaminants.

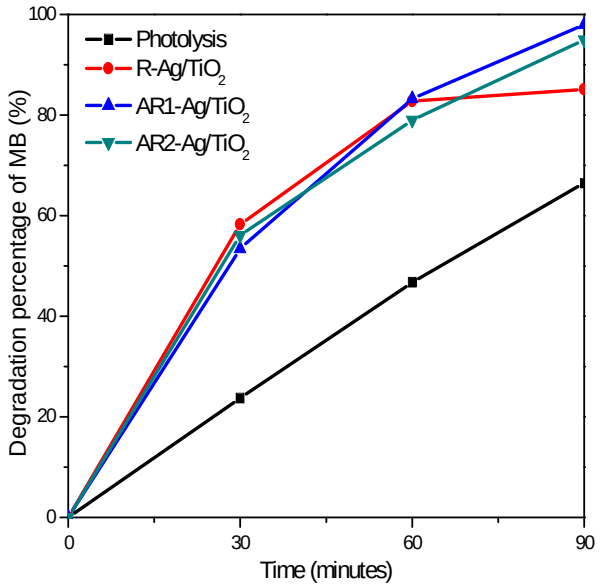

Figure 6: Degradation percentage for photolysis, R-Ag/TiO_2 film and AR-Ag/TiO_2 film prepared at 1 hour and 2 hours

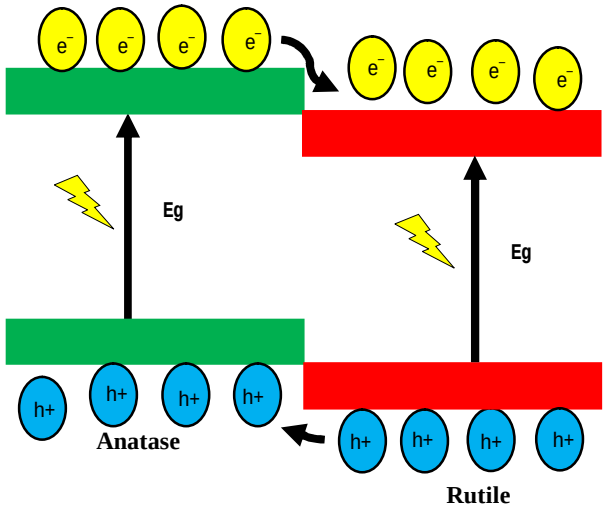

Figure 7: The illustration of electron flow between anatase and rutile phase

5. CONCLUSION

Mixed anatase/rutile Ag doped titanium dioxide (TiO_2) film was successfully fabricated by using two simple steps. This was done to determine the best layer build up anatase nanoparticle decorated on flowerlike Ag doped rutile in TiO_2 and to determine the best degradation rate. The XRD characterization showed the anatase phase peaks were able to be produce on rutile phase by the immersion immersion of tayca 320 solution. Furthermore, the characterization of FESEM showed the flowerlike structure growth on all samples and anatase particle decorated on top of the flowers. The EDX characterization proved there were no foreign elements beside TiO_2. Finally, the photodegradation of AR-Ag/TiO_2 successfully shows the degradation rate of MB. The immersed sample was proven to show successful degradation rate as the methylene blue (MB) dye almost degraded completely in 90 minutes. The optimum immersion of 1 hours shows the best photodegradation and achieved 100 percent degradation in 90 minutes. In conclusion, this project has proven that the simple immersion method can produced mixed anatase/rutile Ag doped titanium dioxide (TiO_2) film for enhance photocatalytic activity. The combination between mixed phase and Ag metal can provide more lifetime to the excited electron that act as electron trapped. Moreover, the decorated anatase also enhance the active surface site for photocatalytic activity take place. This film has a promising properties for waste water treatment for the industries.

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