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Schottky barrier and surface plasmonic resonance phenomena towards the photocatalytic reaction: Study of their mechanisms to enhance the photocatalytic activity

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Abstract

Metals are doped on the semiconductor to enhance the activity of photocatalysts and two possible phenomena can be happened at the interface of the semiconductor: Schottky barrier and Surface Plasmonic Resonance (SPR). Schottky barrier can improve the photoactivity of a reaction by trapping and prolonging the life of electron. While the SPR has the ability to create the electromagnetic field which can improve the photoreaction in three ways: photon scattering, Plasmon Resonance Energy Transfer (PRET) and hot electron excitation. Although both phenomena have been well grounded throughout the field, still one crucial ambiguity is found based on the proposed mechanisms, specifically, what is the direction of electron flow-from metal to semiconductor or vice versa. This feature article reviews the mechanism focusing on how Schottky barrier and the SPR phenomena help to improve a photoreaction as well as the paradox between the Schottky barrier and SPR in the matter of the way of electron flow in the metal/semiconductor system.

1 Introduction

Photocatalyst is a photo-active catalyst which plays a fundamental role to modify the rates of photo-chemical reactions. They have the ability to initiate oxidation and reduction process with the help of incident light on the surface of the catalyst due to the existence of the band gap in the semiconductor. As shown in Figure 1, when the electron in the valance band absorbs photon from a particular wavelength, it is excited to the conduction band, and this excited electron leaves by making a hole in the valance band. Later on, the electrons on the conduction band will move to surface of the catalyst to initiate reduction process, while the holes at the valance band will move to surface to initiate the oxidation process. So far, semiconductor like TiO_2 is proven better in terms of cost, stability and performances compare to other semiconductors, having the large band gap in TiO_2 (3.2 eV) causing the catalyst to work under only the UV and near-UV parts of the solar spectrum .[1]

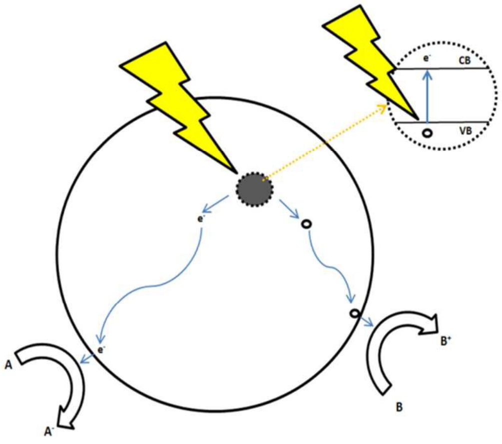

Figure 1. The mechanism of oxidation and reduction process in a photocatalyst

The first observation on the enhancement of metal loading on semiconductor can be traced back to 1980, where Sato et al[2] observed that the photoconversion of H_2O to H_2 and O_2 was increased due to the using of Pt/TiO_2 catalyst system. From that time, extensive researches have focused on the studies of the effect of the noble metal loading on the surface of semiconductor, where this loading will make the Schottky barrier at the interface of the metal-semiconductor [3]. Later on, the application of Surface Plasmon Resonance (SPR) phenomena has been brought into the design of photocatalyst as it is believed that this phenomenon is beneficial in bringing the photocatalyst to be active in visible light region. To initiate both phenomena simultaneously, the requirements (which is very minimum) to be fulfilled, to load the metal on the top of the surface of the semiconductor. However, still there is a great debate, whether the electron is flowing from the semiconductor to the metal due to Schottky Barrier or from the metal to semiconductor due to the SPR effect [4]. It is a critical question in photocatalysis process; therefore, it is highly rational to focus their accepted mechanisms which are available in literature. With this point of view, attempt has been taken and this paper is designed to review the mechanism of Schottky Barrier and SPR effect to surmount the previously mentioned controversy involved with direction of electron flow based on the Schottky Barrier and the SPR effect.

2 Schottky Barrier

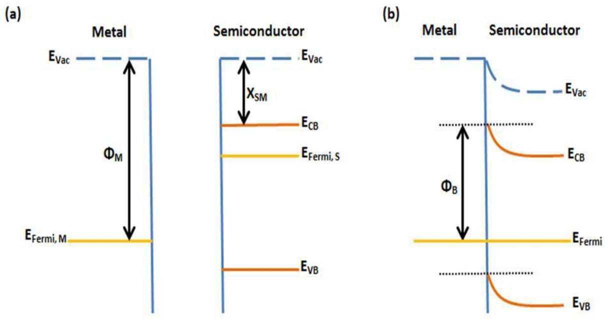

Figure2. Formation of Schottky Barrier between n-type semiconductor and metal (a) before contact and (b) after contact

Figure 2 shows the formation of the Schottky Barrier between an n-type semiconductor and a metal. Within the system, the parameter Φ_M is the working function of the metal, which is defined as the energy needed to bring an electron from the metal Fermi energy to the vacuum. X_{SM} is the electron affinity– the energy difference between the minimum conduction band (CB) and the vacuum (Vac) energy. Usually the metals have a lower Fermi energy (E_{Fermi}) compare to the semiconductor. Preferably, if metal and semiconductor is connected, based on the stability the direction of electron flow will be from the semiconductor to the metal. This flow will be continued until the E_{Fermi} of the semiconductor reaches equilibrium with that of metal, leading to the constant value of E_{Fermi} for both of the devices. Due to this deformation band structure between semiconductor and metal, there is a potential barrier is formed. The electrons (of semiconductor) must overcome that barrier in order to flow from the semiconductor to the metal. This will cause depletion of electron at the semiconductor interface. In another words, there is an accumulation of the negative electron from the metal at the interface, and a formation of the positive space charge layer, or the depletion layer below the surface of the semiconductor in order to maintain electrical neutrality at the interface. This result influences the band bending in the conduction band. This bending (Figure 2) or the Schottky barrier (Φ_B), can be expressed by the following equation:

$$\Phi_B = \Phi_M - X_{SM} \ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad 1$$

Based on the stability concept, the Schottky barrier can serve as an effective electron trapping where the electron is unable to flow back to the semiconductor. This makes the metal to act as the electron sink for the photo-induced electron. The Schottky barrier prevents the recombination of the electron-hole and prolongs the lifespan of the electron for photoreaction [5].

Chiarello *et al.* [6], studied the production of hydrogen in photocatalytic process where the preferred catalysts were Ag/TiO_2, Au/TiO_2, and Pt/TiO_2, and those were activated by methanol photo-steam reforming under 350–450 nm light source. In their study with Ag/TiO_2 catalyst, they observed an increased rate of hydrogen production around fourfold in comparison with P25 TiO_2, while the Au/TiO_2 and Pt/TiO_2 increased the rate by 37 and 52 times, respectively for the same reaction. The authors rationalized the difference in photocatalytic activity of the catalysts by the help of work function values of the metal. They reported the values of work function for Ag, Au, Pt and TiO_2 as 4.74 eV, 5.31, 5.93 and 4.6−4.7 eV, respectively. It is known that the Schottky Barrier will be higher if the difference between metal work function and TiO_2 is larger. Thus, the efficiency of photogenerated electron transfer was increased by trapping the electron into metal, leading to the higher rate of hydrogen production. Likewise, Young *et al.* [7] studied the toluene degradation under UV light irradiation using Ag/TiO_2 and Pt/TiO_2 catalysts. They found that Pt loaded on TiO_2 was able to improve the performance to degrade toluene and mineralizing the intermediates, while the Ag deposited catalyst have negligible effect on its performance. Their interpretation in terms of work function of metals was identical with Chiarello *et al.* [6]. Moreover, it was also suggested that the low work function of Ag compared to TiO_2 leads to minor improvement in photocatalytic performance.

However, Gurunathan [8] tried to load various metals on Bi_2O_3 (band gap 2.8 eV and electron affinity 4.74 eV) via high temperature sintering method to study the relationship between the Schottky barrier and the photocatalytic activity. In his findings, the hydrogen production efficiency under light (with wavelength 350 nm) was increased by following the order of Bi_2O_3 < Cr (IV) < Fe (III) < Ni (II) < Co (II) < Ru (III) < Pd (II). The resulted data of barrier height, work function and photoactivity of his study is summarized in Figure 3.

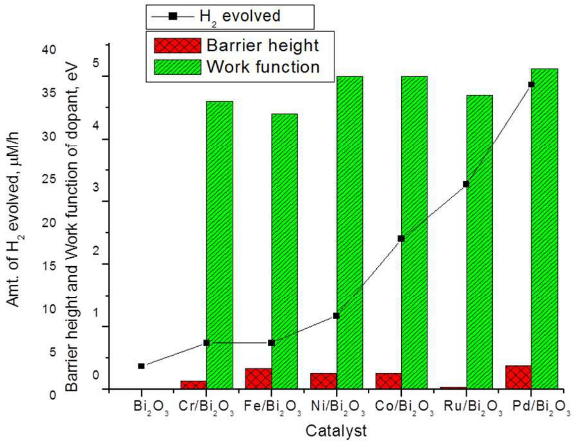

Figure 3. Correlation between the barrier height, work function and the photoactivity (created from Gurunathan [8])

From the Figure 3, it is difficult to find any linear or nonlinear correlation between the barrier height and the photoactivity. It is also interesting to see that metal like Ru (III) having a lower work function (4.71eV) than the electron affinity of Bi_2O_3 (4.74 ev) which was ranked 2nd in hydrogen production. In this case, the work function is lower than the electron affinity, indicates that there is a tendency of the metal not to trap the electron and flowing back to the semiconductor since the barrier is not able to block the electron, rather to flow back to semiconductor. It is important to note that the work function depends on the configurations of atoms at the surface of the material. In his work, the exact state was not confirmed that makes it difficult to correlate the H_2 evaluation data with the work function of the dopants. In addition, it must be noted that the metal has their own catalytic activity towards the surrounding, changing the way of semiconductor to spread the electron into electrolyte [9, 10]. Considering the hydrogen gas production reaction by water splitting, Pt showed the great potential to improve the H_2 gas production; as it can facilitate the electron transfer to water [11, 12]. However, when the reaction is changed from water splitting to glucose reforming for the same H_2 production, Rh is found to give the highest yield followed by Cu, Pt, Ni, Au, Ru, and Ir [13]. For H_2 gas production by water splitting reaction under visible light, Ru loaded on TaON semiconductor is found to have higher yield of H_2 gas compare to Pt, Rh, and Ir loaded semiconductor [14].

On the other hand, the amount of metal loading on the semiconductor should be considered as another influential factor, which can affect the photoactivity. Having more metals on the surface does not mean that there will be more Schottky barrier formed in the system that will benefit the photoactivity. The amount of metal loading is important as it increases the number of electron trapping sites, at the same time reducing the area of the semiconductor exposed to the sunlight itself. According to Shan et al work,[15] when the Ag loading was increased from 1% to 2%, the methyl orange degradation was improved under UV light. Nonetheless, when the Ag loading was further increased from 2% to 3%, the methyl orange degradation was decreased. It might cause that huge number of negative Ag sites can actually attract and recombine positive holes, resulting to lower the photo-activity at the end [16]. Similar phenomena was described by Saktivel *et al.* [17], where they studied the effect of Au, Pt, and Pd loading on TiO_2 towards the degradation of 'acid green 16' and the optimum loading for the Au, Pt and Pd on TiO_2 for the degradation of 'acid green 16' under UV radiation at 254 nm was 0.8%, 0.8% and 0.05% , respectively. As for organic compound degradation, the amount of metal loading is crucial because excessive metal loading on TiO_2 can blockage the TiO_2 defect sites which are necessary for adsorption and photoactivation of oxygen, hence reducing the photoactivity of the organic degradation[18, 19].

3 Surface Plasmonic Resonance

The term Surfaced Plasmon was used in 1957 by Rufus Ritchie. Since then, this term has been used widely in the field of surfaced-enhanced Raman Spectroscopy, Biological Ruler, Nano-scale laser and much more. To the best of our knowledge, the studies on surface plasmon in the photocatalyst can be traced back to 1996 by Zhao *et al.*[20]. Tian *et al.* [19] demonstrated the mechanism of hot electron transfer from the gold to TiO_2, and then SPR effect in photocatalyst was exploited widely and continued to till now. Plasmonic metals like gold, silver and copper and their doping onto semiconductor are widely studied as their surface plasmon can resonate within UV-visible light[21, 22].

Surface plasmon is the collective oscillations of conduction electron at the interface between a conductor and non-conductor [23]. According to Warren *et al.* [24], when an electric field, (for example the solar light), is illuminated on this surface plasmon in the conductor (metal), the electron density is decreased at one side of the conductor and increased at other side. This redistribution of the charge creates an electric field inside and outside of the conductor that is in the opposite direction of electric field. With this electron density displacement, a series of charge densities oscillation will take place and caused by the coulombic restoring force [24]. This phenomenon of charge density oscillation and electric field creation are called Surface Plasmon Resonance (SPR) or Localized Surface Plasmon Resonance (LSPR) [25].

There are three primary mechanisms (shown in Figure 4) that have been identified so far; on how this resonance can help in photoreaction: 1) the scattering of resonant photon by metal, 2) the existence of the intense oscillating electric field around the metal, or can be called as Plasmon Resonance Energy Transfer (PRET) and 3) the production of hot electrons-holes in the metal[26]. There are few literature reviews on the science behind SPR, however Hartland[27] and Warren *et al.*[24] focused the relationship between these mechanisms towards the photoactivity of the reaction.

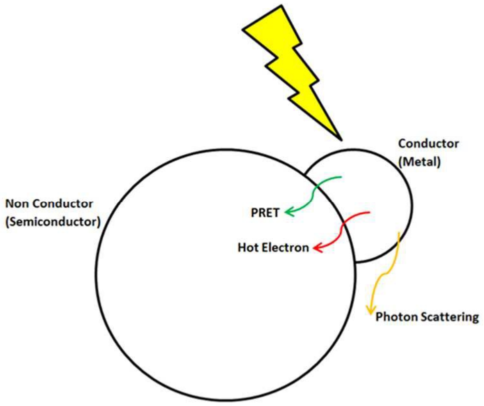

Figure 4. Mechanism initiated by SPR in improving photoreaction

3.1 Photon Scattering

The scattering of light by SPR can be observed directly from our naked eye and its application can be traced back to the old days where the stained glass was made by mixing the metal into the glass, producing a brilliant colourful light on the glass. When the light is illuminated upon the plasmonic nanometal, the metal is able to spread out the incident resonant photons, causing the photons to have longer optical path length to travel around the semiconductor and leading to a higher rate of formation of the charge carrier in semiconductor [26]. In 2010, Christopher *et al.* [28] was able to isolate and verify the improvement of the methylene blue decomposition due to scattering of photon from Ag to TiO_2. In their work the cubic shaped Ag showed higher methylene blue degradation efficiency than the sphere shape Ag under UV light irradiation. This was happened due to the cubic shape Ag could scatter the light much more effectively compare to the sphere shape Ag. The relationship between the size and shape with scattering efficiency of the metal is shown as in Figure 5. As the size of the metal is increased from 30 nm to 100 nm; the metal can scatter the photon more efficiently. Warren *et al.* [24] also mentioned that to maximize the probability of scattering over other effect, the size of the metal at least have to be larger than 100 nm. Moreover, from this Figure, it is also clear that the shape of cubic particles can show better performance than the spherical shaped particles.

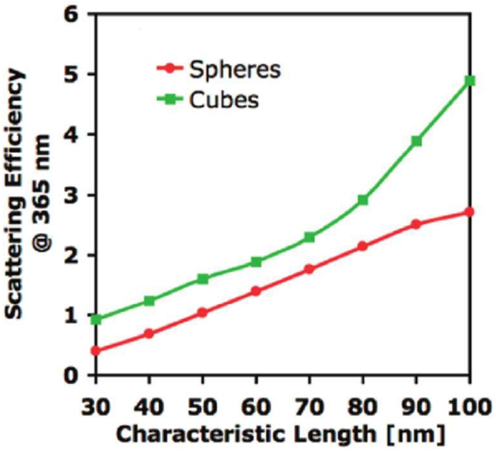

Figure 5. The relationship between the characteristic length of the sphere and cube towards their scattering efficiency calculated using Finite-Difference Time-Domain (FDTD) method at 365 nm[28].

3.2 Plasmon Resonance Energy Transfer

PRET is another mechanism to explain the photoreaction via the existence of the intense oscillating electric field around the metal. According to PRET, the energy is transferred from the plasmon to the absorber (semiconductor) via the electric field. As the light shines on the metal, electric field will be created around the metal and this electric field will promote the rate of formation of electron and holes [29].

In 2007, Awazu *et al.*[30] successfully created plasmonic catalyst consisting Ag core covered by silica shell structure on TiO_2. The Ag-SiO_2 shell was designed to prevent the oxidation of Ag by direct contact of TiO_2. This might happen due to the formation of the opaque silver oxide that prevented Ag to be illuminated to create the electric field. While measuring the photocatalytic activity via methylene blue degradation under near UV light illumination with that catalyst, it was found that the photoactivity increases as the shell thickness decreases. It was estimated that the electric field intensity was decreased exponentially with the distance between metal and semiconductor [31], which was also supported by Kumar *et al.* [32]. In their work, Ag nanoparticle was separated from TiO_2 thin film by SiO_2 interlayer and the effect of SiO_2 interlayer thickness on photocatalytic activity was studied. They also reported that the photoactivity for the methylene blue degradation under UV light illumination was increased as the thickness of SiO_2 interlayer decreased. Torimoto *et al.*[33] prepared composite photocatalysts of CdS nanoparticles immobilized on Au core-SiO_2 shell particles, in which the SiO_2 layer acts as an insulator layer to prevent direct electron transfer from photoexcited CdS to Au particles. Their results confirmed that the enhancement of photocatalytic H_2 evolution was induced by enlargement of the population of excited CdS particles, that is, by photoexcitation of CdS nanoparticles by the LSPR-induced electric fields formed near Au particles. Another reason for the layer coating on the metal nanoparticle is to prevent nanoparticle oxidation to limit the Förster Resonance Energy Transfer , which is the backward reaction of the PRET itself [34].

Furthermore, it is known that the size and shape of the metal have a prominent effect on the electric field produced from the metal. Considering all the factors, to predict the photoactivity of the reaction due to the plasmonic catalyst, Ingram *et al* [26] has developed a predictive model to relate and quantify the photocatalytic reaction with the electric field induced by SPR which is shown as below:

$$\frac{r}{r_0} \propto \int I_0(\lambda) A_{SC}(\lambda) E_{SPR}(\lambda)\, d\lambda \qquad \text{.......2}$$

where r/r_0 is the rate of enhancement of the reaction, I_0 is the wavelength dependent source spectrum, A_{SC} is the semiconductor absorbance spectrum and E_{SPR} is the metal nanoparticle extinction arising from the SPR excitation. With the core concept, the electric field must be able to transfer sufficient energy to overcome the band gap into the semiconductor. They realized that an overlap is needed among the metal SPR spectrum, the semiconductor absorption spectrum, and the illumination source spectrum and this overlapping is directly proportional to photoactivity of a reaction. The overlapping of Source/semiconductor/metal absorbance is presented in Figure 6 which illustrates the proposed model by Ingram *et al.* [26]. From Figure 6, authors stated that the overlapping for Source/N-TiO_2/Ag (Cube) absorbance is larger than Source/N-TiO_2 /Au (Sphere) absorbance. This implies that photoactivity of Ag (cube)/N-TiO_2 is better as compared to Au (sphere)/N-TiO_2. Further, the photoactivity of Ag (cube)/N-TiO_2 and Au (sphere)/N-TiO_2 was compared using methylene blue degradation under broadband of visible light. Indeed, Ag (cube)/N-TiO_2 degraded the methylene blue with better efficiency as compared to Au (sphere)/N-TiO_2, which was in accordance to the model prediction.

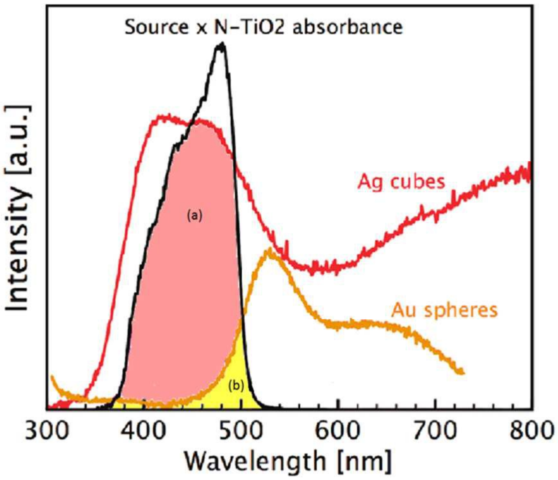

Figure 6. The optical overlapping of the building block for the prediction of photocatalytic activity. (a) Source x N-TiO2 / Ag Cube absorbance overlapping. (b) Source x N-TiO_2 / Au Sphere absorbance overlapping[26]

3.3 Hot Electron Transfer

The third mechanism is the production of hot electrons-holes on the metal. This mechanism is very interesting because instead of the trapping of the electron, some metals are able to supply the electron to the photoreaction under visible light illumination. This mechanism is demonstrated by Tian and Tatsuma.[18, 19] via Au/TiO_2 composite in electrochemical cell as shown in Figure 7, which was supported by several group of researchers such as Wang *et al.*, Zheng *et al.*, and Liu *et al.*, [35-37] where they delivered and explained the photoactivity of metal/TiO_2 photocatalyst under the visible light via this mechanism. However, some researchers[35, 38] still disagree with this mechanism

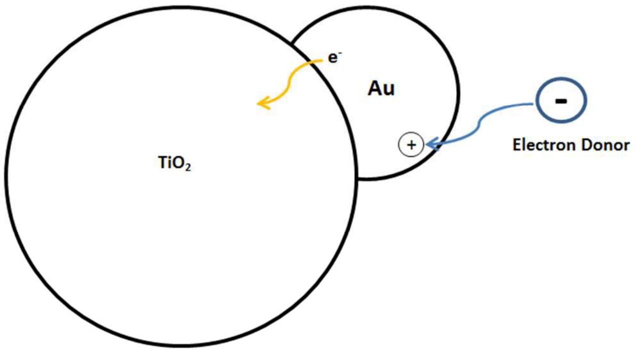

Figure 7: Mechanism of hot electron transfer presented by Tian *et al.* [19]

as it is not consistent with the presence of Schottky Barrier when a metal is contacted with semiconductor. In other words, the function of metal on semiconductor is in doubt whether the metal is supplying the electron to the semiconductors' conduction band, or the metal is trapping the electron from the conduction band. The discussion will be brought forward in the next section. However, the mechanisms of photocatalysis recently studied are summarized in Table 1.

4 Paradox between Schottky barrier and SPR

From the surface, it seems that there is a relationship between the Schottky barrier and the SPR. As mentioned before, when a metal is contacted with a semiconductor, a Schottky barrier is formed between them to trap the electron into the metal, whereas hot electron transfer from metal to semiconductor is visualized through the SPR effect under light irradiation. Till now researchers [39, 40] tried to build a Cu/TiO_2 system which is enable to play both of the functions, and even both of the teams concluded that Schottky barrier is playing more significant role in enhancing the photo-activity of the reaction compare to SPR phenomena.

One major paradox between the Schottky barrier and the SPR is, how the electron is transferred under light illumination. In the context of the Schottky barrier, the excited electron is flowing from the semiconductor, latter on which is trapped inside the metal due to the barrier, prolonging the life of the electron for further reaction. In 2004, Subramaniam *et al.* [41] investigated the charge transfer event from TiO_2 to Au using time-resolved absorption spectroscopy, monitoring the transient absorption decay at 675 nm following 308 nm laser pulse excitation of a deaerated TiO_2 solution. They noticed that the pristine TiO_2 have more intense signal as compared to Au/TiO_2, implying that there are a few amount of electron detected in TiO_2, since most of the electron is transferred to Au. Anpo *et al.* [42] also showed that the electron is photo-generated and transferred from TiO_2 to Pt through Electron Spin Resonance (ESR) signal. The signal intensity of Ti^{3+} for the Pt/TiO_2 is lesser as compared to the TiO_2 catalyst when both catalysts are illuminated under UV light. The electron is transferred to the metal as soon as the electron is trapped on the Ti^{4+} site. In 2006, Emilio *et al.* [43] were also able to use time resolved microwave conductivity (TRMC) to investigate the charge carrier dynamic of the Pt/TiO_2 materials. For the short range of time, TRMC is decayed, resulting a reduction of the signal and its lifetime. Signifying that in this time range, the electrons those are generated by the pulse are deeply trapped in Pt. Disdier *et al.* [44] performed a photoconductivity study on Pt/TiO_2 system, they realized that the conductivity of the Pt/TiO_2 is decreased as compare to the pristine TiO_2 due to the flow of electron from the TiO_2 to the Pt itself.

According to the hot electron and holes mechanism of SPR, the electron is excited from the plasmonic metal due to the SPR effect, latter on which is flowing back inside the TiO_2 conduction band for further reaction. In another word, the metal is functioning as a sensitizer to supply the electron to the semiconductor. To the best of our knowledge, the first proof for this mechanism can be traced back to 2005, when Tian *et al.* [19] studied Au/TiO_2 composite in the electrochemical cell. They claimed that a system containing electrolytes having electron donation capacity, the electron on the gold is photo-excited by SPR effect and transferred from the gold to TiO_2, and the hole left in the gold is replenished from the electron donor in the system itself as shown in Figure 7 [19].

In most of the studies Au has been used as a plasmonic metal rather than the Ag and Cu, to elucidate the hot electron transfer from the metal to semiconductor under sun light irradiation. The important fact is that the surface plasmon on the Au (in general) can resonate under the sunlight as compared to Ag, which resonates under the range of near-UV light region. As instance, for common spherical Au and Ag produced from Sigma-Aldrich, the resonance peak increases from 500 nm to 580 nm [45] and 400 nm to 500 nm [46] when the size increases from 5 nm to 100 nm. Although Cu also shows resonance under sunlight, it can be easily oxidized under ambient condition, losing the metallic properties of Cu itself [47].

A number of studies noted that the electron can be excited from noble metals via SPR [48, 49]. This phenomena can be observed by the naked eye when the gold nanoparticle is supported on TiO_2, the system turns into purple-brown color due to the characteristic surface plasmon band of gold [50]. The change of color on TiO_2 in Au/TiO_2 system suggests the transfer of electron from gold to the conduction band of TiO_2 [19]. Kowalska *et al.* [51] demonstrated the absorption of photons by the Au particles leading to the injection of electron from the excited Au to TiO_2 interface. In 2009, Aprile *et al.* [52] were able to observe the laser excitation of the gold nanoparticle resulting of electron ejection to the medium, where the lifetime of this charge separation is expanding to millisecond time scale. Furube *et al.* [53] showed the flow of SPR excited electron from the gold nanoparticle to TiO_2 nanoparticle using the femtosecond transient absorption spectroscopy. Chen *et al.* [54] quantified the number of electron that obtained sufficient energy to overcome the Schottky barrier via the Fowler Theory. From those studies, they showed that localized SPR promoted the hot electron flow.

Tanaka *et al.* [55] studied the formation of H_2 and acetone from 2-propanol over Au/TiO_2 and Au/TiO_2-Au catalysts under visible light irradiation. Authors found that in Au/TiO_2-Au catalyst two types of Au particles were loaded onto TiO_2, exhibited a larger rate than that of the Au/TiO_2 system which proved that the smaller Au nanoparticle worked efficiently as a co-catalyst. The results of Tanaka *et al.* [55] lead to believe that the larger Au particle (about 13 nm) contributed to strong light absorption for hot-electron excitation, while the smaller Au as electron sinks and becoming the reductive site for the reaction. Shibata *et al.* [56] also mentioned that when Au nanoparticles are very small (< ~ 2nm), they are preferentially attached to specific sites on TiO_2 surface, forming an epitaxial and coherent hetero interface with TiO_2. If the size of gold is larger (> ~ 3nm), the gold-TiO_2 interface loses lattice coherency in order to accommodate the large lattice mismatch between two dissimilar crystals. Kinoyaga *et al.* [57] found that when the diameter of the Au on TiO_2 was increasing from 3 nm to 13 nm, the photoluminescence spectrum of the Au/TiO_2 was decreasing, indicating that reduction of recombination of holes and electron due to the efficient electron transfer from TiO_2 to Au. Gomes Silva *et al.* [58] studied the effect of particle size of Au in Au (0.25 wt%)/TiO_2 towards the hydrogen production from alcohol They realized that Au with diameter of 1.87 nm evolved more oxygen as compared to other Au/TiO_2 catalysts with the diameter of Au larger than 1.87 nm when illuminated under visible light and UV + visible light. They commented that the particle size of the metal affects the distribution of Au nanoparticle with different oxidation potentials on the surface of TiO_2, causing only the fraction of gold nanoparticle fulfills the thermodynamic requirements, where the oxidation potential of those fraction is higher than 1.26 V in order to produce oxygen.

Water splitting has been studied by the irradiation of visible and near-infrared light without certain electron donor due to the efficient charge separation between a metal nanoparticle and a oxide semiconductor[59-64]. The authors explained the enhanced activity over the metal arrayed semiconductor under visible light and near-infrared using by the plasmon induced photogenerated hole based on the hot electron transfer.

Nishijima *et al.* [62] studied plasmon-assisted water oxidation using Au-NRs/TiO_2 electrode and activity was verified by analyzing the evolution of O_2 and H_2O_2 from the electrode. Their results indicated that the stable plasmon-induced electron−hole pairs promote water oxidation. Chen *et al*. [60] reported the mechanism of water splitting over Au-ZnO photoelectrode under visible light using photoelectrochemical cell. Compared to a bare ZnO nanorod photoanode, a Au-ZnO photo- anode has revealed that plasmon induced effects can significantly enhance the overall water splitting. They suggested that the hot electrons that are generated by plasmon damping under visible illumination could be injected into the ZnO over the Schottky barrier, yielding a detectable photocurrent under visible illumination. Authors explained the enhanced photo activity by using the concept of plasmon-induced electromagnetic field evolution near the plasmonic material in the semiconductor which facilitates the separation of electron-hole pairs under the influence of surface potential and effectively enhances the probability of the photochemical reaction associated in the splitting of water.

On the other hand, Chen *et al.* [65] studied the effect of different electromagnetic radiation towards Au/TiO_2 photoactivity in water splitting reaction, and they found no hydrogen and oxygen after illuminating the system for 7 hours. Nonetheless, when the system is illuminated under UV light, the yield of hydrogen and oxygen was 35.04 µmol/g-cat and 17.52 µmol/g-cat respectively. As the system was irradiated under UV and visible light, they noticed that the yield of hydrogen and oxygen was boosted to 53.7504 µmol/g-cat and 25.8704 µmol/g-cat. Tseng *et al.* [29] noticed a similar pattern when comparing the effect the illumination of visible light (about 540 nm), UV light (about 350 nm) and both light onto Au/TiO_2 system towards the methyl orange degradation. Authors also found that the visible light responsive photocatalytic activity of the Au/TiO_2 was not obvious, but when both UV and visible lights were illuminated on the catalyst, the degradation of methyl orange was enhanced significantly as compared to the photoactivity of Au/TiO_2 under UV illumination. These results indicate that the principle of hot-electron transfer mechanism is still in lacking to explain various kinds of situation for Au/TiO_2 itself. If the SPR effect is able to excite electron from the metal, then there should be some activity detected when it is illuminated under visible light as in accordance to the hot electron transfer mechanism. Although the evidence of electron transfer in Au metal is well established, there is still one crucial part that is left out to be examined in details: the whereabouts of the electron after the excitation into the semiconductor conduction band as shown in Figure 8.

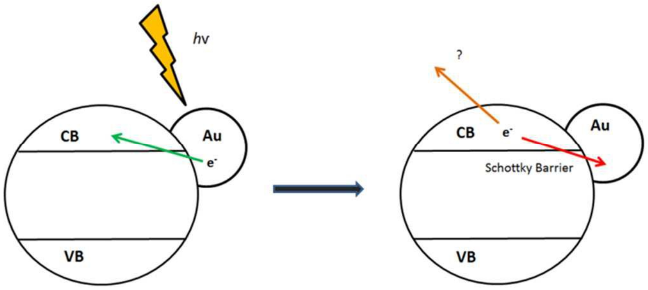

Figure 8. Possible pathway of the electron after being transferred from Au to the conduction band (CB) of TiO_2

Let us assume that under light illumination, due to the SPR effect the electron is injected from the metal to the semiconductor CB. At the same time, as the Schottky barrier exists the electron can easily flow back to the metal. Another thing should be considered, after the excitement of electron on the semiconductor, the nature of the Schottky barrier still exists between Au-TiO_2 interfaces. However, when the metal and the semiconductor are coming into contact, the Fermi levels of both materials will align causing the electron flow to the metal from the semiconductor [66]. In other words, regardless of the origin of the electron, whether it is from the valance band of the semiconductor or the metal, as long as the electron is falling on the conduction band of the semiconductor and the metal is in intact with it. In that condition, the electron will flow towards the metal until the two systems attain equilibrium. In case of Au, due to its high work function, it is able to produce Schottky barrier with high barrier height, facilitating electron transfer into Au as compared to other metals [67, 68]. Kamat [69] reviewed that the double layer charging around gold nanoparticle facilitates storage of electron within the nanoparticle itself. After the excitation of electron from the valance band of TiO_2, the electron will transfer to Au from TiO_2 until two system attained equilibrium. With this accumulation of electron, the Fermi level of Au is increased to more negative potential, shifting the resultant Fermi level of the whole system closer to the conduction band of the semiconductor, thus increasing the reduction power of the photocatalyst. If we link both concepts together logically, there is a tendency where the electron will be circulating around the semiconductor and the gold, which will ended up with the less activity of the photocatalyst. In other word, this hot electron transfer is unable to ensure that all electron excited from gold is participated in the reaction since the presence of the Schottky barrier which send the electron back to the gold itself. Besides that, if the mechanism proposed by the Tian *et al.* [19] is valid, then this will change the role of the gold as photocatalyst instead of TiO_2 since the electron and holes excitation is actually happening at the gold itself.

5 SPR under Visible Light

If the hot electron transfer is not the main mechanism contributing to the photoactivity under visible light, then what will be the mechanism that actually responsible for all the photoactivity that are found under visible light illumination for SPR effect? Rearranging the information that we reviewed so far, Schottky barrier will be out of the topic as Schottky barrier does not shift the band gap, thus unable to promote the excitation of electron under visible light. The main function of the barrier is only to increase the photoactivity by trapping the excited electron into the metal, thus prolonging the lifetime of the electron which is beneficial to the photoreaction. In most of the plasmonic catalyst related studies, it is mentioned that there are photoactivity yield under the illumination of visible light. Later on, SPR phenomena can influence the photoreaction in 3 ways: photon scattering, Plasmon Resonance Energy Transfer, and the hot electron-holes production from the nanoparticle. Photon scattering mechanism does not responsible for the visible light absorption as it only modifies the optical pathway of the photon in the semiconductor. Hot electron production mechanism is not possible as the hot-electron produced will be flowing back to metal itself due to the nature of the Schottky barrier. So what is left after all of the rational deductions indicating to further examine the photoactivity under visible light with Plasmon Resonance Energy Transfer [70-72].

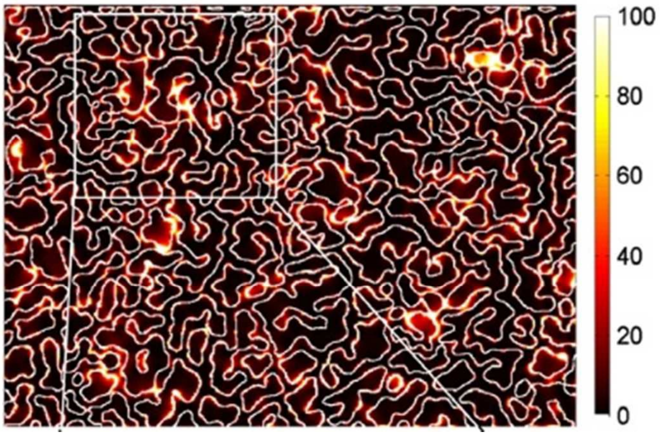

Figure 9. Electric field intensity at the Au/TiO2 interface calculated using FDTD simulation method [73]

According to Warren *et al.* [24], PRET can enhance electric field intensity in a small well defined locations, causing to increase the power absorption in this region. Hou *et al.* [73] defined these locations as the “hot spots”. These hot spots can be seen in Figure 9, where the hot spots are represented by those areas colored by bright yellow. They also added that the electric field intensity in these hot spots can reach up to 1000 times of the incident electric field on the surface of TiO_2 via Finite-Difference Time-Domain (FDTD) simulation study, leading that the photoabsorption and the electron/holes generation rate to be 1000 times more than of normal incident light. One problem faced by n-type TiO_2 is that a relatively thick film is needed to absorb a majority of incident light at λ=550 nm as illustrated in Figure 10(a) [74]. Hou *et al.* [73] added that with the field in the hot spot which is confined in a few nanometer of TiO_2, more electron/holes pair are plasmonic induced around the surface of TiO_2 and participate in the reaction; as compared to the normal TiO_2 where the electron holes pair are far below the surface of TiO_2 to take part in the reaction. In another word, the excitation diffusion length of the plasmonic catalyst is short, allowing the electron hole pair generated to travel safely to surface without undergoing recombination as shown in Fig 10(b) [4].

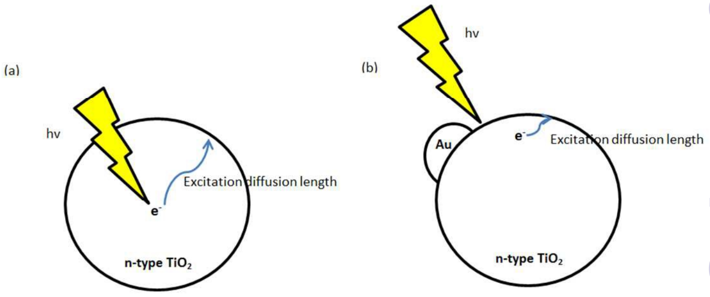

Figure 10. Schematic diagram on excitation diffusion length for (a) bare TiO_2 and (b) Au/TiO_2

According to Hou *et al.* [75], in order to enable the photoactivity under the visible light, the TiO_2 must be doped as to reduce the band gap of the semiconductor so that the semiconductor can be excited to produce the electron under the visible light, later on which is enhanced by PRET where the excitation diffusion path of the electron /holes generated is short. According to the study of Hou *et al.*[73] and Liu *et al.*[70], the band gap excitation of the anodic TiO_2 used in the

Au/anodic TiO_2 system is shifted to a longer wavelength due to nitrogen and fluorine defect produced during anodization which creates a mid-gap state in the forbidden band gap of TiO_2. Ingram *et al*. [26] used the TiO_2 in their Au/TiO_2 system which was doped with the N element to increase the visible light absorption of the semiconductor, leading the photoactivity of the Au/N-TiO_2 to be higher than undoped Au/TiO_2 under visible light irradiation. In contrast to the statement by *Hou et al*. [75], where the TiO_2 semiconductor must be doped in order to reduce the bad gap to enable it to be photoactive under visible light which can be further influenced by the PRET, whereas Ingram *et al*. [26], signifies the role of metal dopant, as well as the light and the semiconductor. So far, the model developed by Ingram *et al.* [26], as discussed in sec 3.2, is the only model which can predict the performance of the metal loaded onto semiconductor photocatalyst towards their photoactivity under light irradiation through the PRET mechanism.

One interesting thing of this model is that there will be photoreaction as long as there is an overlapping between the three spectrums: the source spectrum, metal SPR spectrum and the semiconductor spectrum. There are few factors for making the model by Ingram *et al.* [26] which is more reliable than Hou *et al.* [73] statement. The first point is that this model was developed based on the metal SPR-induced electric field which can supply sufficient energy (the minimum energy required to overcome the band gap) into the nearby semiconductor, hence enabling the excitation of electron from valance band to the conduction band[26].

The resonance peak and the absorbance peak of the plasmonic metal are highly dependent on the size and shape of the metal, making it very hard to generalize and compare all of the metal/TiO_2 photocatalyst. Zhu *et al.* [76] and Dhara *et al*. [77] showed that the LSPR absorption of gold can occur in near UV, visible and near- or mid-infrared regions depending on the size and shape of gold nanoparticle. Kowalska *et al*. [51] showed that the size of the TiO_2 also can affect directly the size of the Au to be deposited on the surface of TiO_2, as well as affect the peak wavelength of the LSPR absorption. Generally, the larger size of TiO_2 particle is associated with the longer peak wavelength of LSPR absorption. By using Ingram *et al*. [26] model, this inconsistency can be overcome by taking the absorbance spectrum of the plasmonic metal that was used into the model itself.

Besides, when the metal is loaded on the surface of TiO_2, there are some possibilities that the metal will be doped into the lattice of TiO_2 depending on the methods used, making the TiO_2 to be visible light active. Taking Au/TiO_2 photocatalyst as an example, Melinte *et al.* [78] reduced the band gap of TiO_2 from 3.00 eV to 2.86 eV and 2.88 eV by soaking the TiO_2 aerogel with 22 nm and 5 nm Au colloidal nanoparticle, respectively. Zhou *et al.* [79] created Au/TiO_2 system through a simple spray hydrolytic method using photoreduction technique at 90˚C, causing the Au/TiO_2 to have a slight red shift in band gap transition as compared to the pristine TiO_2. Using acetic acid hydrolyzed sol gel method, Loganathan *et al.* [80] shifted the band gap excitation of TiO_2 to a longer wavelength by increasing the amount of Au in the Au/TiO_2 system. However, Jose *et al.* [4] prepared the Au/TiO_2 system with solvated atom dispersion model method, they found that the band gap of the TiO_2 did not shift before and after Au loading on TiO_2.

6. Summery and Outlook

The current paper reviews the role of metal into semiconductor to enhance the photoactivity of the metal/semiconductor system. The mechanisms related to metal/semiconductor have been proposed in the literature such as Schottky barrier and SPR: photon scattering, PRET and hot electron transfer mechanism are reviewed in this paper. Although the fundamental of the Schottky barrier towards the photoactivity has been well established, but the mechanisms of SPR in photoactivity enhancement still remain inconsistence throughout the field. Based on the information that we reviewed so far, it could be concluded that the electron is indeed excited from the metal to TiO_2 via hot electron mechanism. Although, the whereabouts of the electron after it is transferred to the conduction band is in doubt as following the basic law of Schottky barrier, electrons are supposed to transfer to metal afterward. It is also believed that instead of hot electron transfer, PRET mechanism by SPR is the main mechanism which caused TiO_2 to be photoactive under visible light where the photoactivity of any reaction depends on the optical spectrum of the semiconductor, metal and the light source. Based on the so far observed literature, it is possible to state that all of the proposed hypotheses are very conceptual. After all, it is important to understand and verify the photoactivity mechanism of metal-semiconductor system so that design of the photocatalyst can be improved in future.

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Notes and References

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