

# Determination of the Band Gap and Intensity of Palladium/Silver Doped TiO<sub>2</sub> Nano Particles Using Diffuse Reflectance and Photoluminescence Spectra

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**Abstract:** The photocatalysts Pd/TiO<sub>2</sub>, Ag/TiO<sub>2</sub> and Ag/Pd-TiO<sub>2</sub> were prepared using the sol immobilization method. The photocatalysts were characterized by the use of diffuse reflectance spectra (DRS) and photoluminescence spectra. Analysis of Ag/TiO<sub>2</sub> and Ag/Pd-TiO<sub>2</sub> using diffuse reflectance spectra (DRS) indicated reduction of band gap energy from 3.2 eV to 2.7 eV for Ag/Pd-TiO<sub>2</sub> which makes it possible for the use of sunlight as excitation energy. Photo luminescence spectra analysis carried out on the dopants of Ag/TiO<sub>2</sub>, Pd/TiO<sub>2</sub> and Ag/Pd-TiO<sub>2</sub> measured the intensity which gives the rate of recombination of photo-generated electron-hole pairs in TiO<sub>2</sub>. The result indicated that reduction in intensity was highest for the co-doped Ag/Pd-TiO<sub>2</sub>. This accounts for its increase in photo catalytic property. Therefore, modification of TiO<sub>2</sub> with Ag and Pd will provide the platform for its enhanced photocatalytic performance relevant in environmental science.

**Keywords:** Sol immobilization; photoluminescence; band gap; intensity; Ag/Pd-TiO<sub>2</sub>.

## 1. Introduction

Titanium, the ninth most common element in the Earth's crust, naturally interacts with oxygen to form titanium dioxide (TiO<sub>2</sub>). For over a century, the diverse applications of TiO<sub>2</sub> range from the industrial to consumer products [1]. However, among other applications, the performance of TiO<sub>2</sub> as a semiconductor and photocatalyst (in thin film, powder or nanostructured layer) in environmental photocatalysis application is remarkable in degradation of toxic organic compounds of health concern [2 - 5].

Photocatalysis applications of TiO<sub>2</sub> result from a low cost, availability, biological and chemical inertness, good optoelectronic properties and favourable photoactivity [6-8]. But the anticipated photocatalytic potentials of TiO<sub>2</sub> has the following setbacks: (1) A wide band gap (3.2 eV for anatase and 3.0 eV for rutile corresponding to wavelengths of 385 and 410 nm respectively) that limits the excitation strictly to UV light irradiation [9-12]. TiO<sub>2</sub> cannot efficiently utilize solar light since UV light is only 4-6% of solar radiation; (2) A high recombination rate of photogenerated electron and hole pairs that leads to low

photonic efficiency, which in turn slows down the photocatalytic reactions [9,13-14].

In order to beat these limitations, the coupling of semiconductor photocatalysts with noble metals such as Ag, Au, Pd and Pt has proved to be the most promising strategy. This results due to the shift in the irradiation wavelength from the UV to the visible range (380 and 780 nm) [15-16, 17].

Therefore, the determination of band gap is essential for identification of the changes in the electronic structures of titanium dioxide after deposition with noble metals such as silver and palladium; to signal the efficiency of its performance when used as a photocatalyst. Diffuse reflectance spectroscopy (DRS) is an effective spectroscopic tool for determining the band gap of microcrystalline materials.

Kubelka-Munk theory provides the theoretical descriptions of DRS [18]. When a powdered sample is radiated with light, a portion is regularly reflected at its surface and the remaining enters the powder and diffuses. As light of a particular wavelength is absorbed by the sample, measurement of diffuse reflected light at different wavelength yield a spectrum called diffused reflectance spectrum.

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The intensity of the diffused reflectance spectrum in the limiting case of infinitely thick sample is effectively expressed by Kubelka-Munk equation [19].

$$k/s = \frac{(1 - R_{\infty})^2}{2R} = F(R_1)$$

Where  $R_1$  is the absolute diffuse reflectance (KubelkaMunk Function),  $K$  = absorption coefficient and  $S$  = scattering coefficient which varies with particle size and packing,  $R$  = the ratio of the reflection from the sample to the intensity of reflection from a standard sample.

In practice the measure of reflective diffuse reflectance ( $R$ ) gives the ratio of the reflection from the sample to the intensity of reflection from a standard sample. Furthermore, photoluminescence measures the rate at which electron moves from conduction band to valence band (intensity) [20].

This study is therefore aimed in determining the effect of doping on the band gap of palladium/silver doped  $\text{TiO}_2$  nano particles, by measuring the intensity of the spectra. This is imperative towards assessing the superiority of mono- and di-doping of  $\text{TiO}_2$  nanoparticle for efficient and effective photocatalytic performance.

## 2. Materials and Methods

### Preparation of $\text{Ag/TiO}_2$ and $\text{Pd/TiO}_2$ catalyst

The catalysts used were prepared using sol immobilisation method as reported by Yilleng (2018) [21], with a few modifications. Standard sol-immobilization method was utilised to prepare the Ag, Pd, Ag-Pd nano particles supported on  $\text{TiO}_2$ . The supported silver and silver-palladium colloids were prepared by using Polyvinyl alcohol (PVA) as protective ligand, aqueous solutions of  $0.005 \text{ mol/dm}^3 \text{ PdCl}_2$  and  $0.006 \text{ mol/dm}^3 \text{ AgNO}_3$  were prepared.

Then a 1.0 wt % aqueous PVA, (Aldrich, MW = 10000, 80% hydrolysed) solution was freshly prepared just prior to synthesis of the metal colloid. A representative protocol for preparing a catalyst comprising of Ag-Pd nano-particles with 1 wt % total metal loading on a  $\text{TiO}_2$  was carried out as follows; To an aqueous  $0.005 \text{ mol/dm}^3 \text{ PdCl}_2$  and  $0.006$

$\text{mol/dm}^3 \text{ AgNO}_3$  solution,  $100 \text{ cm}^3$  of PVA solution (1 wt %) was added (PVA/ (Ag and Pd) (w/w) = 1.2). Then a freshly prepared solution of  $\text{NaBH}_4$  ( $0.1 \text{ M}$ ,  $\text{NaBH}_4$ / (Ag and Pd) (mol/mol) = 5) was added to form a dark brown sol.

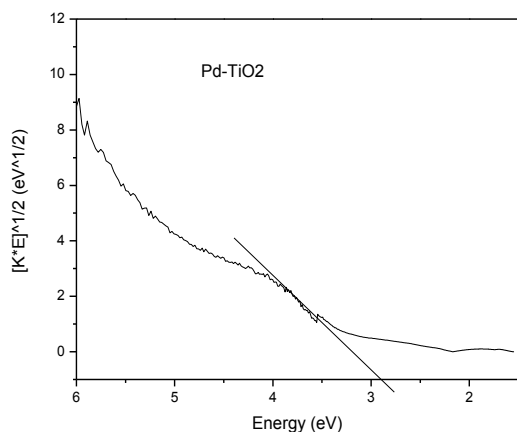
After 30 min of sol generation, the colloid was immobilised by adding  $\text{TiO}_2$  (acidified to pH 1-2 by using tetraoxosulphate (VI) acid) with vigorous stirring with a glass rod. The amount of support material required was calculated to have a total final metal loading of 1 wt %. After 2 hours, the slurry was filtered and the catalyst washed thoroughly with distilled water (neutral mother liquors) and dried at  $120^\circ\text{C}$  overnight in an oven. Sol immobilised mono-metallic silver and palladium catalysts were prepared using similar procedure.

$\text{Pd/TiO}_2$ ,  $\text{Ag/TiO}_2$  and  $\text{Ag/Pd-TiO}_2$  were characterized using Jasco V-570 UV-VIS-NIR spectro photometer monitored under the wavelength range of 200 nm - 800 nm. Photoluminescence (PL) measurement were carried out on a Horiba John Yvon- flouromax 4. The excitation wavelength used was 385 nm and the emission spectra were monitored at 320 - 520 nm range.

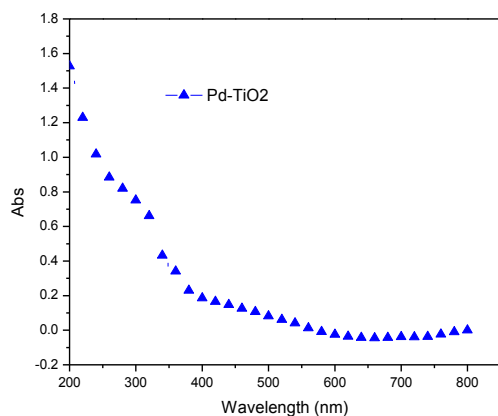
## 3. Result and Discussion

### Diffusion reflectance spectroscopy (DRS) spectra of 0.5% $\text{Pd/TiO}_2$ catalyst

The absorption of Pd doped  $\text{TiO}_2$  is presented in Fig. 1, this consists of a single broad intense absorption band at the range of 400 – 440 nm which can be attributed to the charge transfer from the valence band to the conduction band which on calculation using Kubelka-Munk function in Fig. 2, gives the Band gap energy for  $\text{Pd-TiO}_2$  as 2.84 eV. The modified catalyst exhibits a slight red shift (the band gap excitation was slightly shifted to longer wavelengths) in the band transition from the normal value of 3.2 eV for P25 on adding the Pd metal.



**Fig. 1** Diffuse reflectance spectra of 0.5% Pd-TiO<sub>2</sub>.



**Fig. 2** Kubelka-Munk function diagram of 0.5% Pd-TiO<sub>2</sub> for the band gap energy.

Shon *et al.* (2007) reported that doping Ag with TiO<sub>2</sub> creates new energy levels between the valence band and conduction band of TiO<sub>2</sub> which in turn reduces its band gap and helps the doped catalyst to absorb at visible light region [22]. This was attributed to the fact that the visible light photocatalytic activity is associated with the red shift that originate from the creation of local bands between the VB and CB of nano-crystalline titanium dioxide [22].

The result of this study is also similar to that of Baroro *et al.* (2012), in which doping Pt and Ag ion TiO<sub>2</sub> enhance the electron-hole separation by acting as electron traps which extend the light absorption into the visible range and enhance surface electron excitation by plasmon resonances excited by visible light [23].

In addition, according to Zhang *et al.* (2009), Pt/TiO<sub>2</sub> had lower band gap than that of undoped TiO<sub>2</sub> by about 0.2 eV and showed

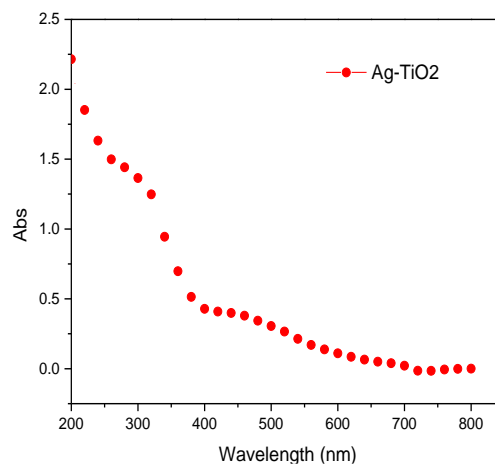
higher photocatalytic efficiency than undoped TiO<sub>2</sub> [24]. Therefore, the doping of TiO<sub>2</sub> with Ag and Pd enhances the absorption of light in the visible region and so can improve its photocatalytic potentials for utilization in environmental clean-up of organic pollutants.

### Diffusion reflectance spectroscopy (DRS) spectra of 0.5% Ag/TiO<sub>2</sub> catalyst

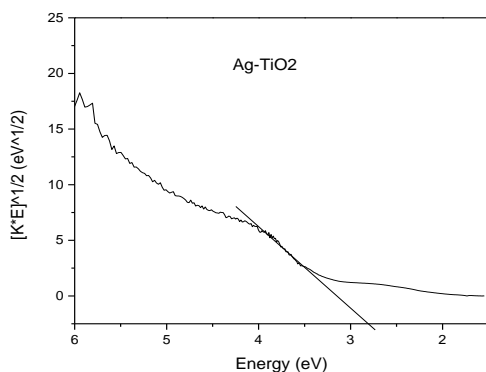
The DRS spectra of Ag/TiO<sub>2</sub> presented in Fig. 3 consist of a broad band spectrum of intense absorption at range between 300 – 400 nm for Pd-TiO<sub>2</sub>. The Kubelka–Munk function in Fig. 4 gives 2.9 eV band gap energy which really improves the photocatalytic performance of Ag/TiO<sub>2</sub>. Therefore, Ag/TiO<sub>2</sub> has strong interaction with pure-TiO<sub>2</sub>, as well as Pd/TiO<sub>2</sub> as indicated in the band gap energy.

The reduction in band gap energy implies that the problem of visible light response of TiO<sub>2</sub> was overcome by metal doping with Ag and Pd. The result is in line with previous studies that doping of TiO<sub>2</sub> with other metals is a promising method to achieve visible light response of TiO<sub>2</sub>.

The result shows that the excited Ag and Pd centers donate electron to the TiO<sub>2</sub> conduction band (CB), which can allow the oxidation of surface adsorbed molecules like organic pollutants. This was accounted for by the work of Wu *et al.*, (2004); with the report that Vanadium doped TiO<sub>2</sub> show quite high photocatalytic property under visible light irradiation. It is believed that under visible light, the excited Vanadium centers donate electron to the TiO<sub>2</sub> CB, which allows the oxidation of surface adsorbed molecules [25].



**Fig. 3** The diffuse reflectance spectra of 0.5% of Ag-TiO<sub>2</sub>.



**Fig. 4** Kulbeka-Munk function diagram of 0.5% Ag-TiO<sub>2</sub> for the band gap energy.

#### Diffusion reflectance spectroscopy (DRS) spectra of 0.5% Ag/Pd-TiO<sub>2</sub> catalyst

The absorption spectrum of Ag/Pd-TiO<sub>2</sub> presented in Fig. 5, indicated intense absorption at range of 300 – 400 nm which after calculation using Kulbeka-Munk function and its spectra in Fig. 6 gave a band gap energy of 2.735 eV.

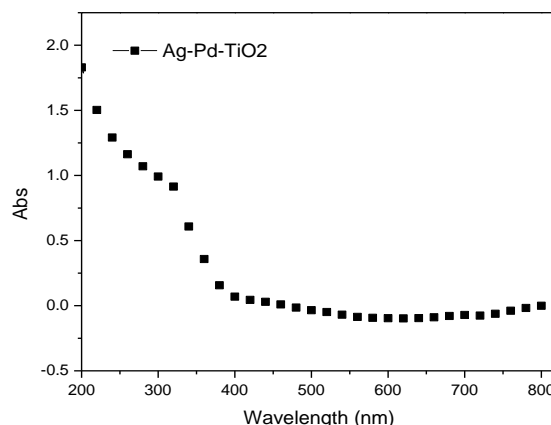
Therefore, from the diffusion reflectance spectroscopy spectrum and the Kulbeka-Munk function diagram of Pd/TiO<sub>2</sub>, Ag/TiO<sub>2</sub> and Pd/Ag-TiO<sub>2</sub> in this study, it is inferred that bimetallic co-doping (Ag-Pd-TiO<sub>2</sub>) shift the absorption to lower band gap energy, thereby making the absorption to take place within the visible light region instead of the ultraviolet region, when compared to that of single metallic doping Ag/TiO<sub>2</sub> and Pd/TiO<sub>2</sub>. The report is in agreement with the work of Ahmed *et al.* (2013) [26].

Also, the result of this study using Pd/TiO<sub>2</sub>, Ag/TiO<sub>2</sub> and Pd/Ag-TiO<sub>2</sub> shows that bimetallic doping with Pd and Ag shift the absorption to lower band gap energy thereby making the absorption to take place in the visible light region as asserted by Zang *et al.* (2009) [24].

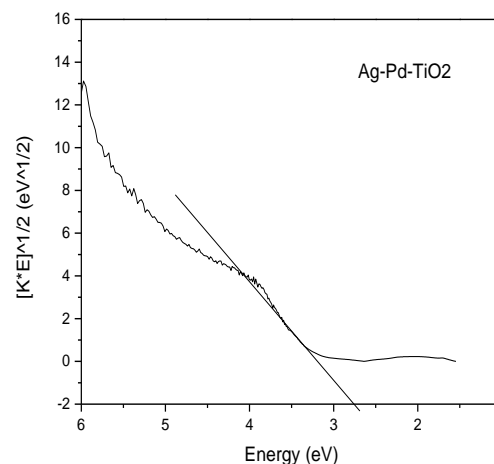
The main benefit of doping is that high percentage of the anatase phase is exhibited from the XRD result of the prepared catalyst, as reported in the previous work carried by the team [27], and phase transformation of the anatase phase to the rutile phase is inhibited [28].

As depicted in Fig. 6, Ag/Pd-TiO<sub>2</sub> shows higher reduction in band gap energy compared to Pd-TiO<sub>2</sub> and Ag/TiO<sub>2</sub>. The reduction was from 3.02 eV to 2.7 eV for Ag/Pd-TiO<sub>2</sub>, and 2.9 eV to 2.8 eV for Pd/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> respectively.

Therefore, Ag/Pd-TiO<sub>2</sub> has the highest photocatalytic activity compared to the mono doped Pd/TiO<sub>2</sub> and Ag/TiO<sub>2</sub> dopants.



**Fig. 5** The diffuse reflectance spectra of 0.5% Ag/Pd-TiO<sub>2</sub>.



**Fig. 6** Kulbeka-Munk function diagram of 0.5% Ag/Pd-TiO<sub>2</sub> for the band gap energy.

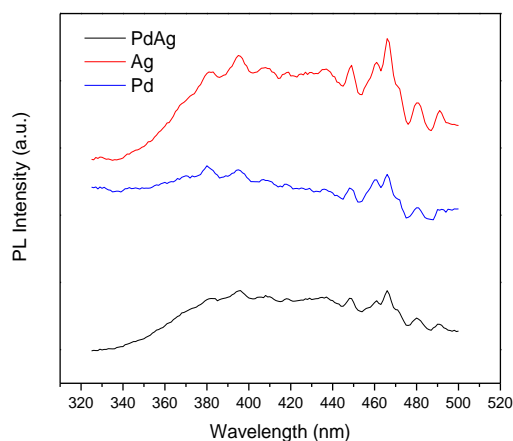
#### The Photoluminescence emission spectra of 0.5% Ag/TiO<sub>2</sub>, Pd/TiO<sub>2</sub> and Pd/Ag-TiO<sub>2</sub>

The separation efficiencies of the photo-generated holes and electrons can be determined by photoluminescence emission spectra, in which lower PL emission intensity shows decrease in recombination rate of the charge carriers. Following from Fig. 7, the photoluminescence emission spectra of the prepared samples indicated that Ag/TiO<sub>2</sub> dopant has the highest intensity with a very broad peak maximum at 450 nm followed by Pd/TiO<sub>2</sub> dopant and Pd/Ag doped TiO<sub>2</sub>. Pd/TiO<sub>2</sub> show a very broad peak maximum close to 460 nm while Pd/Ag-TiO<sub>2</sub> has a broad peak maximum close to 465 nm. The intensity

of the dopant decreases from Ag/TiO<sub>2</sub> to Pd/TiO<sub>2</sub> with Pd/Ag-TiO<sub>2</sub> recording the least.

Ag doped TiO<sub>2</sub> has the highest intensity because of the recombination of electron as it moves from valence band (VB) to conduction band (CB) [23]. Pd/Ag-TiO<sub>2</sub> has the lowest intensity because of retardation of the electron recombination from conduction band to valence band due to the capture of electron by the Pd-Ag doped on TiO<sub>2</sub>. The co-doped transition metal traps the electron and prevents it from falling back to the valence band where electron hole is created.

Based on the results in Fig. 7, the PL intensity of Pd/Ag-TiO<sub>2</sub> sample significantly decreased relative to those of Pd-TiO<sub>2</sub> and Ag-TiO<sub>2</sub>, indicating a lower recombination rate for the photogenerated electrons and holes of Pd/Ag-TiO<sub>2</sub>. Importantly, the decreased charge carrier recombination is in favour of the enhanced photocatalytic activity of the catalysts.



**Fig. 7** Combined photoluminescence emission spectra of 0.5% Pd/TiO<sub>2</sub>, Ag/TiO<sub>2</sub> and 0.5% Pd/Ag-TiO<sub>2</sub>.

#### 4. Conclusion

The diffuse reflectance spectra analysis indicated that there was remarkable reduction in the band gap for bimetal dopants of Pd/Ag-TiO<sub>2</sub> compared to the monometal dopants (Ag/TiO<sub>2</sub> and Pd-TiO<sub>2</sub>), this enables the doped TiO<sub>2</sub> to absorb at the visible light region thereby increasing the photocatalytic activity.

The photoluminescence spectra analysis also shows that Pd/Ag-TiO<sub>2</sub> has lower intensity than Ag/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> dopants, thereby leading to a decrease in the rate of

recombination of excited electron from the valence band to conduction band and thus could increase the rate of its photocatalysis of organic pollutants.

Therefore, the presence of the metal ion dopant Ag/Pd in the crystalline TiO<sub>2</sub> could significantly influence the photo reactivity by changing charge carrier recombination rates and interfacial electron transfer rates, so shifting the band gap of the catalyst into the visible region. Ag/Pd TiO<sub>2</sub> dopant ion act as an electron trap or hole trap. This prolongs the life time of the generated charge carriers, resulting in an enhancement in photocatalytic activity. Ag/Pd-TiO<sub>2</sub> is a promising photocatalyst and can find relevance in environmental science.

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