

Determination of the Band Gap and Intensity of Palladium/Silver Doped TiO₂ Nano Particles Using Diffuse Reflectance and Photoluminescence Spectra

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Abstract: The photocatalysts Pd/TiO₂, Ag/TiO₂ and Ag/Pd-TiO₂ 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/TiO₂ and Ag/Pd-TiO₂ using diffuse reflectance spectra (DRS) indicated reduction of band gap energy from 3.2 eV to 2.7 eV for Ag/Pd-TiO₂ which makes it possible for the use of sunlight as excitation energy. Photo luminescence spectra analysis carried out on the dopants of Ag/TiO₂, Pd/TiO₂ and Ag/Pd-TiO₂ measured the intensity which gives the rate of recombination of photo-generated electron-hole pairs in TiO₂. The result indicated that reduction in intensity was highest for the co-doped Ag/Pd-TiO₂. This accounts for its increase in photo catalytic property. Therefore, modification of TiO₂ 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-TiO₂.

1. Introduction

Titanium, the ninth most common element in the Earth's crust, naturally interacts with oxygen to form titanium dioxide (TiO₂). For over a century, the diverse applications of TiO₂ range from the industrial to consumer products [1]. However, among other applications, the performance of TiO₂ 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 TiO₂ result from a low cost, availability, biological and chemical inertness, good optoelectronic properties and favourable photoactivity [6-8]. But the anticipated photocatalytic potentials of TiO₂ 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]. TiO₂ 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.

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 TiO_2 nano particles, by measuring the intensity of the spectra. This is imperative towards assessing the superiority of mono- and di-doping of TiO_2 nanoparticle for efficient and effective photocatalytic performance.

2. Materials and Methods

Preparation of Ag/TiO_2 and 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 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 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 cm^3 of PVA solution (1 wt %) was added (PVA/ (Ag and Pd) (w/w) = 1.2). Then a freshly prepared solution of NaBH_4 (0.1 M , 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 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°C overnight in an oven. Sol immobilised mono-metallic silver and palladium catalysts were prepared using similar procedure.

Pd/TiO_2 , Ag/TiO_2 and 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% Pd/TiO_2 catalyst

The absorption of Pd doped 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 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.

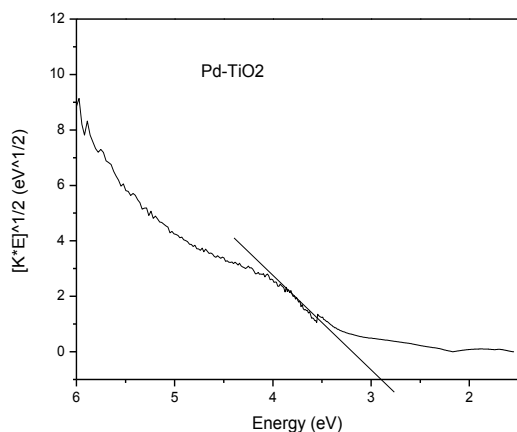


Fig. 1 Diffuse reflectance spectra of 0.5% Pd-TiO₂.

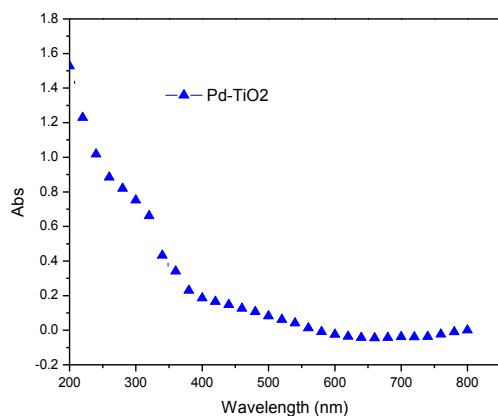


Fig. 2 Kubelka-Munk function diagram of 0.5% Pd-TiO₂ for the band gap energy.

Shon *et al.* (2007) reported that doping Ag with TiO₂ creates new energy levels between the valence band and conduction band of TiO₂ 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 TiO₂ 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/TiO₂ had lower band gap than that of undoped TiO₂ by about 0.2 eV and showed

higher photocatalytic efficiency than undoped TiO₂ [24]. Therefore, the doping of TiO₂ 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/TiO₂ catalyst

The DRS spectra of Ag/TiO₂ presented in Fig. 3 consist of a broad band spectrum of intense absorption at range between 300 – 400 nm for Pd-TiO₂. The Kubelka–Munk function in Fig. 4 gives 2.9 eV band gap energy which really improves the photocatalytic performance of Ag/TiO₂. Therefore, Ag/TiO₂ has strong interaction with pure-TiO₂, as well as Pd/TiO₂ as indicated in the band gap energy.

The reduction in band gap energy implies that the problem of visible light response of TiO₂ was overcome by metal doping with Ag and Pd. The result is in line with previous studies that doping of TiO₂ with other metals is a promising method to achieve visible light response of TiO₂.

The result shows that the excited Ag and Pd centers donate electron to the TiO₂ 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 TiO₂ show quite high photocatalytic property under visible light irradiation. It is believed that under visible light, the excited Vanadium centers donate electron to the TiO₂ CB, which allows the oxidation of surface adsorbed molecules [25].

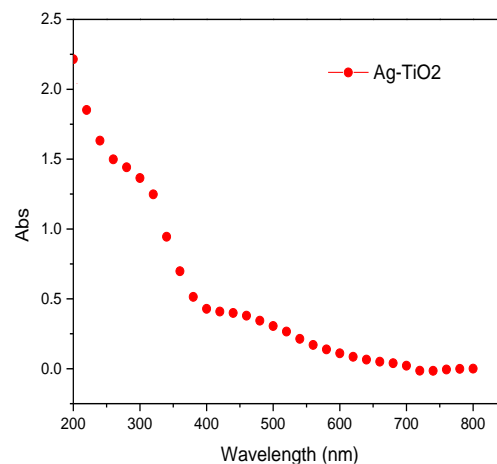


Fig. 3 The diffuse reflectance spectra of 0.5% of Ag-TiO₂.

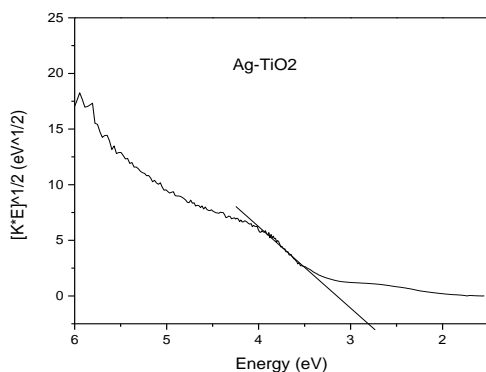


Fig. 4 Kulbeka-Munk function diagram of 0.5% Ag-TiO₂ for the band gap energy.

Diffusion reflectance spectroscopy (DRS) spectra of 0.5% Ag/Pd-TiO₂ catalyst

The absorption spectrum of Ag/Pd-TiO₂ 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/TiO₂, Ag/TiO₂ and Pd/Ag-TiO₂ in this study, it is inferred that bimetallic co-doping (Ag-Pd-TiO₂) 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/TiO₂ and Pd/TiO₂. The report is in agreement with the work of Ahmed *et al.* (2013) [26].

Also, the result of this study using Pd/TiO₂, Ag/TiO₂ and Pd/Ag-TiO₂ 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-TiO₂ shows higher reduction in band gap energy compared to Pd-TiO₂ and Ag/TiO₂. The reduction was from 3.02 eV to 2.7 eV for Ag/Pd-TiO₂, and 2.9 eV to 2.8 eV for Pd/TiO₂ and Ag/TiO₂ respectively.

Therefore, Ag/Pd-TiO₂ has the highest photocatalytic activity compared to the mono doped Pd/TiO₂ and Ag/TiO₂ dopants.

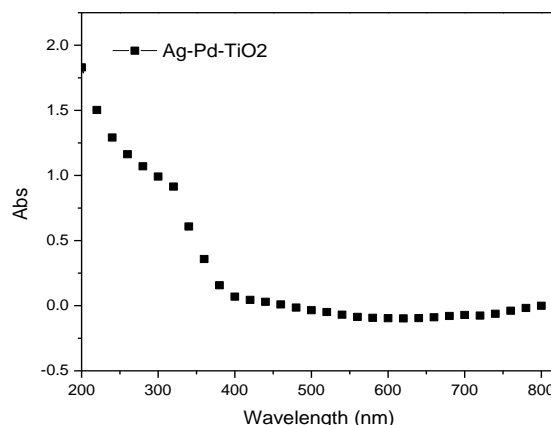


Fig. 5 The diffuse reflectance spectra of 0.5% Ag/Pd-TiO₂.

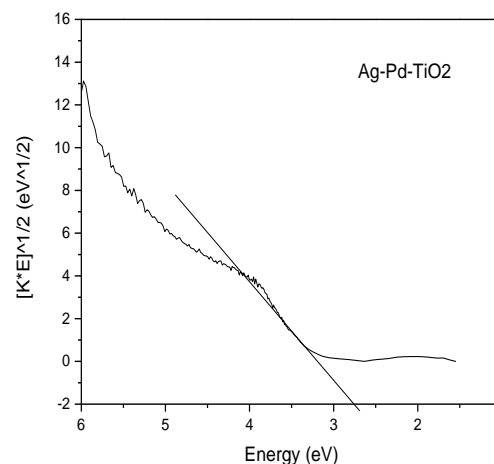


Fig. 6 Kulbeka-Munk function diagram of 0.5% Ag/Pd-TiO₂ for the band gap energy.

The Photoluminescence emission spectra of 0.5% Ag/TiO₂, Pd/TiO₂ and Pd/Ag-TiO₂

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/TiO₂ dopant has the highest intensity with a very broad peak maximum at 450 nm followed by Pd/TiO₂ dopant and Pd/Ag doped TiO₂. Pd/TiO₂ show a very broad peak maximum close to 460 nm while Pd/Ag-TiO₂ has a broad peak maximum close to 465 nm. The intensity

of the dopant decreases from Ag/TiO₂ to Pd/TiO₂ with Pd/Ag-TiO₂ recording the least.

Ag doped TiO₂ has the highest intensity because of the recombination of electron as it moves from valence band (VB) to conduction band (CB) [23]. Pd/Ag-TiO₂ 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 TiO₂. 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-TiO₂ sample significantly decreased relative to those of Pd-TiO₂ and Ag-TiO₂, indicating a lower recombination rate for the photogenerated electrons and holes of Pd/Ag-TiO₂. Importantly, the decreased charge carrier recombination is in favour of the enhanced photocatalytic activity of the catalysts.

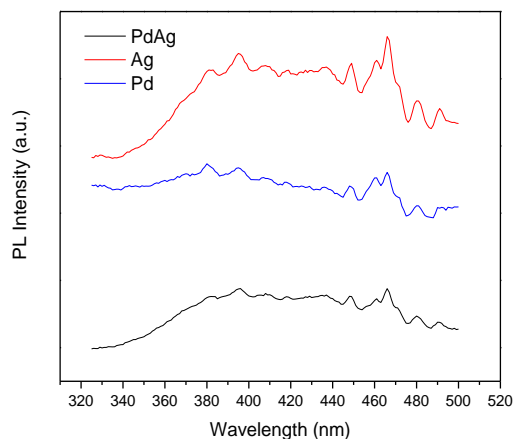


Fig. 7 Combined photoluminescence emission spectra of 0.5% Pd/TiO₂, Ag/TiO₂ and 0.5% Pd/Ag-TiO₂.

4. Conclusion

The diffuse reflectance spectra analysis indicated that there was remarkable reduction in the band gap for bimetal dopants of Pd/Ag-TiO₂ compared to the monometal dopants (Ag/TiO₂ and Pd-TiO₂), this enables the doped TiO₂ to absorb at the visible light region thereby increasing the photocatalytic activity.

The photoluminescence spectra analysis also shows that Pd/Ag-TiO₂ has lower intensity than Ag/TiO₂ and Pd/TiO₂ 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 TiO₂ 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 TiO₂ 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-TiO₂ is a promising photocatalyst and can find relevance in environmental science.

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