

# Fabrication of Several Metal-Doped TiO<sub>2</sub> Nanoparticles and Their Physical Properties for Photocatalysis in Energy and Environmental Applications

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**Abstract:** Heterogeneous TiO<sub>2</sub> photocatalysis is widely used in various ways in environmental and energy fields, including water and air purifications, self-cleaning surfaces, photocatalytic reaction, and hydrogen production. In this work, silver (Ag), copper (Cu), and rubidium (Rb) at various contents (1 wt%, 3 wt%, and 5 wt. %) were used as metals for doping on commercial TiO<sub>2</sub> nanoparticles by impregnation technique. All samples were calcined under air (400°C for 3 h). The structural characteristics and optical property of metal-doped TiO<sub>2</sub> nanoparticles were characterized by field emission scanning electron microscopy (FESEM), UV-visible (UV-vis) spectroscopy, and photoluminescence (PL) spectroscopy. From FESEM, it was found that pristine TiO<sub>2</sub> showed low agglomeration, while metal-doped TiO<sub>2</sub> at high metal content showed more agglomeration. From UV-vis reflection spectra, it was found that increase in content of metal in TiO<sub>2</sub> nanoparticles resulted in lower reflectance. These results are in line with PL spectra. PL intensity reduced with increasing metal content. It was found that 5 wt. % Cu-doped TiO<sub>2</sub> showed the lowest PL intensity, implied low electron-hole recombination rate (good property for enhancement of photocatalytic activity of the materials). It can be concluded that metal-doped TiO<sub>2</sub> nanoparticles are promising materials to be utilized as photocatalysts for various energy and environmental applications.

**Keywords:** metal doping, TiO<sub>2</sub>, light absorption, photoluminescence.

## 1. Introduction

Over past several years, semiconductor materials have shown great potential for fuel production and environmental remediation. Uses of various types of semiconductor, such as Ge, GaAs, CdS, ZnO, and TiO<sub>2</sub> were introduced to many applications which were fundamentally interesting. However, they showed both advantages and disadvantages depending on the applications [1].

Titanium dioxide or titania (TiO<sub>2</sub>) is one of well-known semiconductors, which is able to be activated under light irradiation and used as a catalyst in several chemical processes. It also has attracted considerable attention in energy and environmental fields. Its optical appearance is a white solid inorganic and it occurs in form of rock and sand in nature. Normally, TiO<sub>2</sub> has 3 metastable phases, i.e. anatase, rutile, and brookite, which anatase phase has been reported to be more active than rutile and brookite [2]. However, crude TiO<sub>2</sub> nanoparticles are amorphous in nature. So, it still has some limitations such as relatively wide energy band gap, high rate in recombination of electron and hole, and inefficient utilization in visible light [3].

To improve the efficiency of TiO<sub>2</sub>, elimination of the limitations as mentioned above has been studied. Many studies have been reported to modify TiO<sub>2</sub>, such as changes of size (i.e. nano- and micro-sized TiO<sub>2</sub>), variation of shape (i.e. particle, tube, plate, and mesoporous), dye addition, variation of crystalline composition (i.e. anatase/rutile ratio), coating and doping (i.e. metal, ion, and metal/ion dopes).

The doping of metals into TiO<sub>2</sub> is an effective way to improve the performance of the catalyst. This method can

reduce the band-gap energy and reduce electron-hole recombination rate. This can promote the separation of photogenerated charge carriers and shift light absorption from UV region to visible region [4].

A large number of studies have been carried out to modify catalyst for utilizations in many applications. Recently, there are many works have studied on metal-doped TiO<sub>2</sub>. Doping of metal ion in a semiconductor is known to affect both photophysical behavior and photochemical reactivity [5].

Gupta et al. [6] reported the structural and optical properties of pristine TiO<sub>2</sub> and Ag (3% and 7% wt.) doped TiO<sub>2</sub>. Prepared samples were characterized by X-ray diffractometer (XRD), transmission electron microscope (TEM), UV-vis spectrophotometer, and photoluminescence (PL) spectrometer. They found that the pristine TiO<sub>2</sub> nanoparticles showed poor ability in degradation of bacteria (microbial application), while doping of silver ions can improve the efficiency of the degradation of bacteria under visible-light irradiation. Various applications of Ag-doped TiO<sub>2</sub> have achieved much attention. For examples, Coto et al. [7] studied the degradation of methylene blue under visible light irradiation with synthesized Ag-TiO<sub>2</sub>. Rather et al. [8] reported hydrogen (H<sub>2</sub>) production from water via Ag-TiO<sub>2</sub> nanorods under visible light irradiation.

For other metals, Cu is also one of interesting and extensive metal for doping of TiO<sub>2</sub>. For examples, Khemthong et al. [9] studied the structures and properties of modified TiO<sub>2</sub> nanorods with Cu at 1, 3, 5, 7 and 10 wt. %. Prepared samples were characterized using various techniques, including XRD, BET, XAS, TEM, and UV-DRS. Cu-doped TiO<sub>2</sub> nanorods at mind content were found to be remarkable and efficient catalysts in their study. Rb is an alkali metal that is interesting. However,

there have been only a few studies of Rb metal-doped TiO<sub>2</sub> [10]. There is no one carried out the comparison of modifications of TiO<sub>2</sub> nanoparticles by quite expensive metals (i.e. Ag and Cu) and alkali metals (i.e. Rb).

In this paper, we modified TiO<sub>2</sub> with Ag, Cu, and Rb at mind concentrations (1, 3, and 5 wt. %). The physical properties were systematically studied by FESEM, UV-vis spectroscopy, and PL spectroscopy. This work will fulfill the steps of ongoing efforts for development of modified semiconductor photocatalysts for energy and environmental applications which is workable under visible light.

## 2. Experimental

### 2.1 Preparation of metal-doped TiO<sub>2</sub> powders

Metal (Ag, Cu, or Rb) doped TiO<sub>2</sub> as catalysts in this experiment were modified by impregnation technique using TiO<sub>2</sub> nanoparticles (AEROXIDE®, TiO<sub>2</sub>) as based material which was purchased from Acros Co. (Belgium), silver nitrate (AgNO<sub>3</sub>), copper nitrate (Cu (NO<sub>3</sub>)<sub>2</sub>), and rubidium nitrate (RbNO<sub>3</sub>) were purchased from Wako Pure Chemical Industries, Ltd. (Japan). Deionized water was produced in Quantum Energy Processes Laboratory, Graduate School of Energy Science, Kyoto University. Certain amounts of AgNO<sub>3</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, and RbNO<sub>3</sub> (for 1%, 3% and 5% wt. of Ag, Cu, and Rb in the synthesized samples) dissolved in deionized water (8 mL) was added dropwise on TiO<sub>2</sub> powders. Then, the solutions were mixed and stirred until they became homogeneous. All catalysts were dried at 60 °C for 24 h and calcined at 400°C for 4 h. After that, the separation of size was carried out by sieves to obtain the same size of metal-TiO<sub>2</sub> nanoparticles. In this work, the maximum metal doping was only 5% wt., because it was reported that the optimized doping content in photocatalytic applications is not over 5% wt. [6,9]. The properties of lower band gap and high recombination of electron/hole with metal doping have to be compromised.

### 2.2 Characterizations of metal-doped TiO<sub>2</sub> powders

Microstructure, morphological appearance, and agglomeration of pristine TiO<sub>2</sub> and metal-doped TiO<sub>2</sub> samples in this study were characterized by field emission scanning

electron microscopy (FESEM, Hitachi SU-6600). The magnification was at 15,000x to see the particles at the same time with agglomerations.

The optical reflectivity of the produced powders has been measured by a JASCO V-550 UV-vis spectrophotometer in the wavelength range of 200–800 nm. BaSO<sub>4</sub> was used as a reference.

PL spectra of prepared samples were investigated by a PL spectrometer (JASCO FP-8600). This experiment was performed at room temperature. An excitation was accomplished with 270 nm and interval wavelength is in the range of 350 to 600 nm.

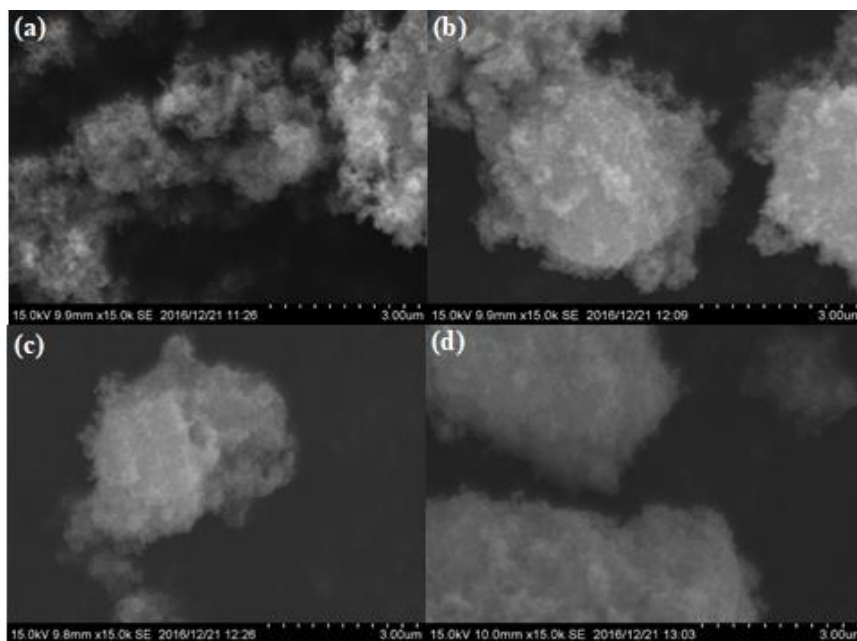
## 3. Results and Discussion

### 3.1 Sample morphological appearance

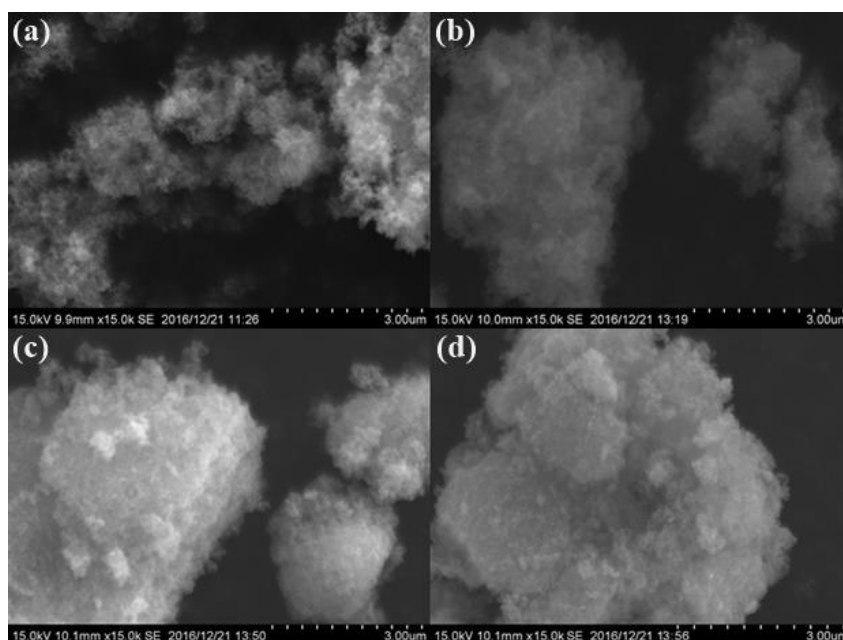
FESEM has been conducted to observe the morphology of samples with different contents of Ag-TiO<sub>2</sub>. Morphology of pristine TiO<sub>2</sub> is compared with Ag-doped TiO<sub>2</sub> at 1%, 3% and 5%wt, as shown in Figures 1(a-d). The surface morphology of samples was found to change after metal doping, i.e. pristine TiO<sub>2</sub> showed low agglomerations, but all Ag-doped TiO<sub>2</sub> samples shows relatively higher agglomerations and extended particle clusters. This is due to originality of impregnation technique leads to some agglomerations on the surface.

Figures 2(a-d) show FESEM images of pristine TiO<sub>2</sub> and Cu-doped TiO<sub>2</sub> at 1%, 3% and 5%wt. The figures show the morphology and agglomeration of the prepared catalysts. Pristine TiO<sub>2</sub> showed low agglomeration while Cu-doped showed irregular particle cluster structures, relatively same with the case of Ag-doped samples in Figure 1. This figure clearly indicates that the Cu doping may cause some changes in properties of the obtained samples.

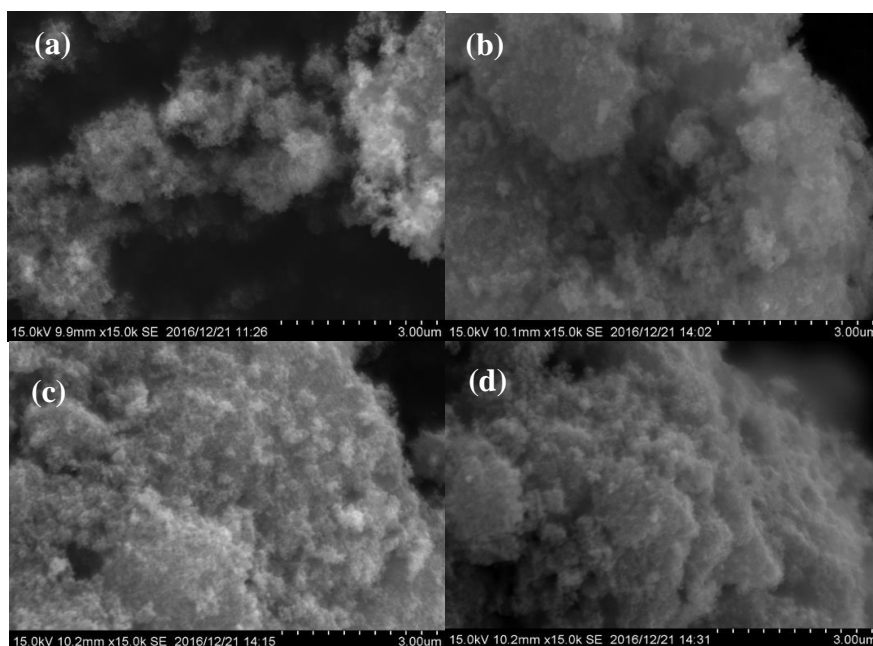
FESEM images of pristine TiO<sub>2</sub> and Rb-doped TiO<sub>2</sub> at 1%, 3%, and 5%wt. are depicted in Figures 3(a-d), respectively. It can be seen that sponge-like network of particle clusters is sufficiently demonstrated after doping with Rb. Surface roughness and shaped complexity of the particles is high in case of high Rb-TiO<sub>2</sub>. Because of impregnation technique, Rb may not be uniformly deposited on the surface of TiO<sub>2</sub> nanoparticles.



**Figure 1.** FESEM images of catalysts (a) pristine TiO<sub>2</sub>, (b) 1% Ag-TiO<sub>2</sub>, (c) 3% Ag-TiO<sub>2</sub>, and (d) 5% Ag-TiO<sub>2</sub> at 15.0 k magnification.



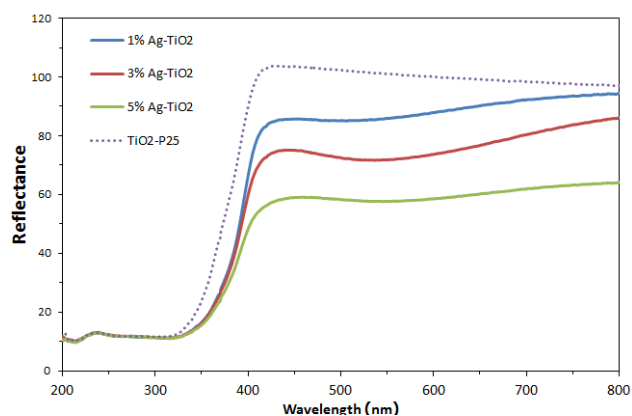
**Figure 2.** FESEM images of (a) pristine TiO<sub>2</sub>, (b) 1% Cu-TiO<sub>2</sub>, (c) 3% Cu-TiO<sub>2</sub>, and (d) 5% Cu-TiO<sub>2</sub> at 15.0 k magnification.



**Figure 3.** FESEM images of (a) pristine TiO<sub>2</sub>, (b) 1% Ru-TiO<sub>2</sub>, (c) 3% Ru-TiO<sub>2</sub>, and (d) 5% Ru-TiO<sub>2</sub> at 15.0 k magnification.

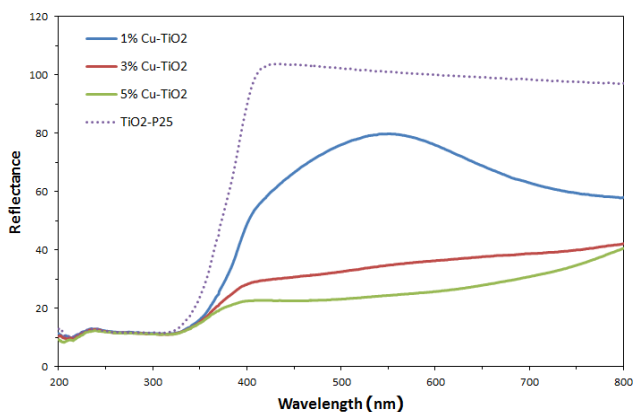
### 3.2 UV-vis diffuse reflectance

Reflectance spectra of pristine TiO<sub>2</sub> and Ag-doped TiO<sub>2</sub> at various Ag contents (1, 3, and 5 wt. %) are shown in Figure 4. Normally, the energy band gap of TiO<sub>2</sub> is approximately 3.2 eV [11] which coincide to the UV absorption at wavelengths around 390 nm. From this work, it can be seen that the Ag-doped TiO<sub>2</sub> reached a broad absorption band in visible region, in the range of wavelength more than 400 nm. The reason of this expression is the fermi level of Ag is lower than TiO<sub>2</sub> [12] and photoexcited electrons in conduction band can be transferred to the dopant particles that located on the surface of TiO<sub>2</sub>, while photogenerated holes in valence band remain in the TiO<sub>2</sub>. Moreover, increasing of Ag content increase an absorption in visible region (resulted in darker colors in the obtained catalysts) [13]. So, it can be concluded that Ag-doped TiO<sub>2</sub> extends its absorption into the visible region, especially 5% Ag-doped TiO<sub>2</sub>.



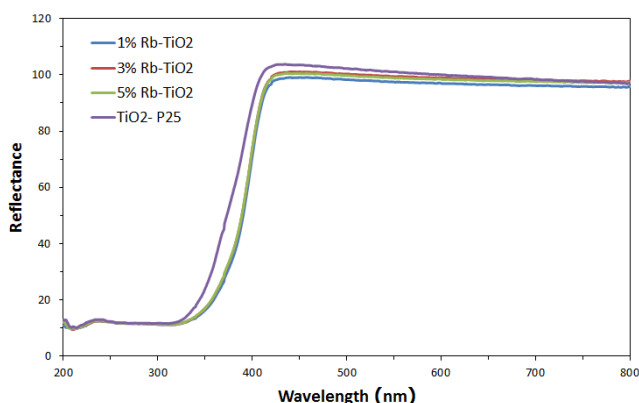
**Figure 4.** The diffuse reflectance spectra from UV-vis spectrophotometer of (a) pristine TiO<sub>2</sub>, (b) 1% Ag-TiO<sub>2</sub>, (c) 3% Ag-TiO<sub>2</sub>, and (d) 5% Ag-TiO<sub>2</sub>.

Figure 5 shows UV-vis reflective spectra of pristine TiO<sub>2</sub> and Cu-doped TiO<sub>2</sub> at various Cu contents (1, 3, and 5 wt. %). The pristine TiO<sub>2</sub> shows the strong absorption band around 350 nm corresponding to TiO<sub>2</sub>. The Cu-doped TiO<sub>2</sub> exhibited a large absorption band between 400 nm and 700 nm, especially with an increase in Cu content (resulted in darker colors in the obtained catalysts). This is because the light absorption in the visible region (400 to 700 nm) is achieved by the absorption of Cu<sub>2</sub>O and CuO on the TiO<sub>2</sub> surface, due to Cu<sub>2</sub>O and CuO (P-type semiconductors) have band gaps of around 2.1 and 1.7 eV, respectively [14]. So, it can be concluded that Cu modified TiO<sub>2</sub> also extends the light absorption into the visible region, especially 5% Cu-doped TiO<sub>2</sub>.



**Figure 5.** The diffuse reflectance spectra from UV-vis spectrophotometer of (a) pristine TiO<sub>2</sub>, (b) 1% Cu-TiO<sub>2</sub>, (c) 3% Cu-TiO<sub>2</sub>, and (d) 5% Cu-TiO<sub>2</sub>.

The optical properties of pristine and Rb-doped TiO<sub>2</sub> at various contents were examined by UV-vis spectrophotometer as shown in Figure 6. It was found that Rb-doped TiO<sub>2</sub> at various contents (1, 3, and 5 wt. %) were not significant different with each other. Moreover, Rb-doped TiO<sub>2</sub> samples are only slightly red-shifted compared with the pristine TiO<sub>2</sub>. Not same with Ag-doped TiO<sub>2</sub> and Cu-doped TiO<sub>2</sub> catalysts, Rb-doped TiO<sub>2</sub> showed not significant change in the color with increasing concentration (the color was white in all samples). It can be concluded that surface-modification of TiO<sub>2</sub> by Rb doping does not significantly change optical property of the absorption in the visible region.



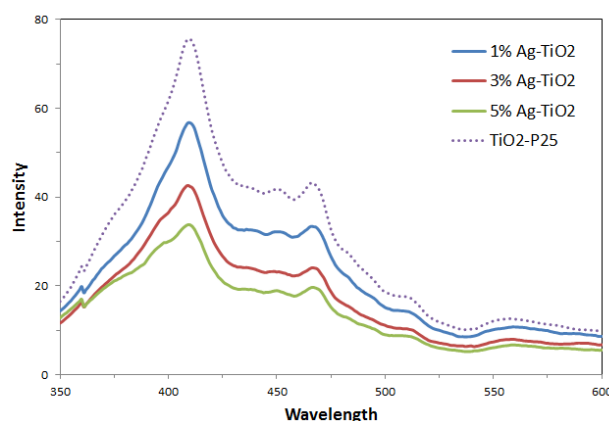
**Figure 6.** The diffuse reflectance spectra from UV-vis spectrophotometer of (a) pristine TiO<sub>2</sub>, (b) 1% Rb-TiO<sub>2</sub>, (c) 3% Rb-TiO<sub>2</sub>, and (d) 5% Rb-TiO<sub>2</sub>.

### 3.3 Photoluminescence

To further investigate and understand effects of TiO<sub>2</sub> surface modification by metals at different doping contents (1, 3, and 5 wt. % of Ag, Cu, and Rb), PL spectra of pristine TiO<sub>2</sub> and

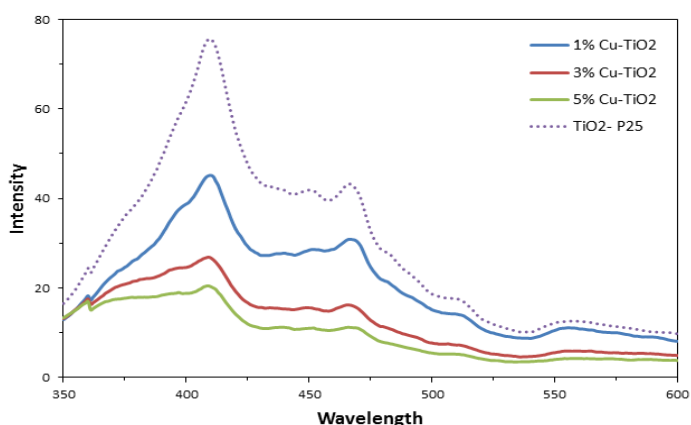
metal-doped TiO<sub>2</sub> samples were obtained and discussed, because PL spectra can indicate the recombination processes, migration, and transfer of photo-generated electron-hole pairs in semiconductors [6].

Figure 7 shows PL spectra of Ag-doped TiO<sub>2</sub> at 1, 3, and 5 wt.% compared with pristine TiO<sub>2</sub>. It can be observed that the intensity of Ag-modified TiO<sub>2</sub> catalyst were lower in comparison to pristine TiO<sub>2</sub> because the metallic silver ions can affect in some changes in the electronic structure of the Ag-doped TiO<sub>2</sub> [15]. Especially at the highest content (5 wt. %), it shows the lowest PL intensity, meaning delays in recombination rate.



**Figure 7.** PL spectra of (a) pristine TiO<sub>2</sub>, (b) 1% Ag-TiO<sub>2</sub>, (c) 3% Ag-TiO<sub>2</sub>, and (d) 5% Ag-TiO<sub>2</sub>.

PL emission spectra of the TiO<sub>2</sub> and Cu-doped TiO<sub>2</sub> at 1, 3, and 5 wt. % are shown in Figure 8. Pristine TiO<sub>2</sub> exhibited the highest PL intensity, indicating the highest recombination rate of electrons and holes [16]. After Cu ions were doped on the surface of TiO<sub>2</sub>, the intensity of the PL spectra decrease. That is because the peaks of Cu-doped TiO<sub>2</sub> indicated the radiative transition of the excited electrons from occupied d bands to higher states of the Fermi level [17]. Especially, the emission intensity of Cu-doped TiO<sub>2</sub> at 5 wt.% shows the lowest intensity, which indicated the lowest recombination rate of photogenerated charges.



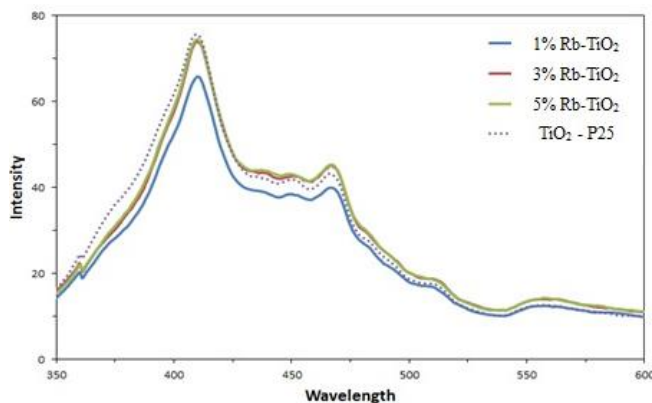
**Figure 8.** PL spectra of (a) pristine TiO<sub>2</sub>, (b) 1% Cu-TiO<sub>2</sub>, (c) 3% Cu-TiO<sub>2</sub>, and (d) 5% Cu-TiO<sub>2</sub>.

PL emission spectra of the TiO<sub>2</sub> and Rb-doped TiO<sub>2</sub> are shown in Figure 9. The PL results confirmed relative importance of the modification of TiO<sub>2</sub> by Rb for hindering the recombination of electrons and holes at 1% Rb doping. Anyhow, Rb-doped TiO<sub>2</sub> at higher contents (3 and 5 wt. %) were not significantly different in intensities compared with the pristine TiO<sub>2</sub>.

**Table 1.** Comparison of properties of pristine TiO<sub>2</sub> and metal doped TiO<sub>2</sub> at different metal types (Ag, Cu, and Rb) and contents (1%, 3%, and 5%).

Sample	Doping contents (%)	Morphology	Light absorption wavelength edge (visible absorption increase from pristine TiO <sub>2</sub> ) <sup>a</sup>	PL intensity at ~412 nm (a.u.)
TiO <sub>2</sub>	-	Particles in small cluster	339 nm (n/a)	75
Ag-doped TiO <sub>2</sub>	1	Agglomerations with irregular particle cluster	352 nm (20%)	56
	3	Agglomerations with irregular particle cluster	359 nm (30%)	42
	5	Agglomerations with irregular particle cluster	354 nm (50%)	33
Cu-doped TiO <sub>2</sub>	1	Agglomerations with irregular particle cluster	363 nm (30%)	45
	3	Agglomerations with irregular particle cluster	376 nm (70%)	27
	5	Agglomerations with irregular particle cluster	382 nm (80%)	20
Rb-doped TiO <sub>2</sub>	1	Sponge-like particle cluster	348 nm (5%)	66
	3	Sponge-like particle cluster	348 nm (5%)	74
	5	Sponge-like particle cluster	348 nm (5%)	74

<sup>a</sup> “Visible absorption increase from pristine TiO<sub>2</sub>” refers to more absorption in visible light region compared with pristine TiO<sub>2</sub>.



**Figure 9.** PL spectra of (a) pristine TiO<sub>2</sub>, (b) 1% Rb-TiO<sub>2</sub>, (c) 3% Rb-TiO<sub>2</sub>, and (d) 5% Rb-TiO<sub>2</sub>

### 3.4 Comparison of various metal types and contents in TiO<sub>2</sub> modifications

All properties of pristine TiO<sub>2</sub> and metal doped TiO<sub>2</sub> at different metal types (Ag, Cu, and Rb) and content (1%, 3%, and 5%) are summarized in Table 1 for comparison. It was found that high content of metal-doped TiO<sub>2</sub> affect the surface of catalyst, in which more agglomeration with irregular and sponge-like particle cluster were found. Light absorption of Ag- and Cu-doped catalysts showed increases from pristine TiO<sub>2</sub>, especially 5% Cu-doped TiO<sub>2</sub> that showed the highest visible absorption. Rb-doped samples, however, showed not significant changes. The light absorption was in line with intensity of PL spectra, which higher Ag and Cu doping showed lower PL intensity, referring to lower recombination of electrons and holes. The lowest PL intensities of Ag and Cu were at 5% doping. On the other hand, in case of Rb, high contents of Rb in doped TiO<sub>2</sub> (3% and 5%) did not significantly change the PL peaks of pristine TiO<sub>2</sub>.

From all results, it can be concluded that the modification of surface of TiO<sub>2</sub> by metals has effect in performance of light absorption and electronic states (recombination of electrons and holes) of materials which will further affect ability and activity of obtained catalysts.

## 4. Conclusions

Silver (Ag), copper (Cu), and rubidium (Rb) at various contents (1, 3, and 5 wt%) were used as metals for doping on commercial TiO<sub>2</sub> nanoparticles by impregnation technique. The structural characteristics and optical property of metal-doped TiO<sub>2</sub> nanoparticles were characterized by field emission scanning electron microscopy (FESEM), UV-visible (UV-vis) spectroscopy, and photoluminescence spectroscopy (PL). It was found that low agglomeration was shown in pristine TiO<sub>2</sub> and the agglomeration trended to be higher when TiO<sub>2</sub> was modified by metals. Increase in content of metals in TiO<sub>2</sub> nanoparticles resulted in higher UV-vis light absorption. These results are in line with PL spectra, because PL intensity reduced with increasing metal content. Moreover, 5 wt% Cu-TiO<sub>2</sub> showed the lowest PL intensity when compared with all of materials in this work, implied low electron-hole recombination rate (good property for enhancement of photocatalytic activity of the materials). It can be concluded that metal-doped TiO<sub>2</sub> nanoparticles are promising materials to be utilized as photocatalysts for various energy and environmental applications. The variations of morphology, light absorption, and electronic states in metal-doped TiO<sub>2</sub> in this work open the ways to adjust physical properties and photocatalytic activity of photocatalysts in the actual applications.

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