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Characterization and Photocatalytic Efficiency of Palladium Doped-TiO_2 Nanoparticles

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ABSTRACT

The effect of modification of TiO_2 with different palladium concentrations on its characteristics and photocatalytic efficiency was studied. Photo catalysts were prepared by the sol-gel method and were characterized by different techniques. A uniform distribution of palladium through the TiO_2 matrix was observed. The X-ray diffraction patterns of the pure and palladium doped TiO_2 were found to be quiet similar and the average particle size was not significantly changed. As a result of palladium doping, the UV-Vis analysis showed a red shift in the onset of wavelength of absorbance and the band gap was changed from 3.39 to 3.06 eV for the 0.3 wt% Pd/TiO_2 sample. Photo catalytic removal study of formic acid showed that the 0.3 wt% palladium doped photocatalyst exhibits the highest efficiency among the different palladium doped photocatalysts using sun light as the radiation source.

Keywords: TiO_2 Nanoparticles; Sol-Gel Process; Thermal Analysis; Photocatalyst; and Formic Acid

1. Introduction

Titanium dioxide (TiO_2) has been widely used as a photocatalyst for degrading a wide range of organic compounds [1]. In addition, TiO_2 has attracted extensive interests because of its potential applications to photocatalysis [2], chemical sensors [3], solar cell electrodes [4], and hydrogen storage materials [5]. However, the TiO_2 photocatalyst is known to have limitations for practical applications. One of these limitations is that the TiO_2 has activity only under light of wavelength shorter than 388 nm because of its wide band gap (Eg = 3.2 eV) [6-8]. The wide band gap limits the use of sunlight as excitation energy and the high rate of recombination of photo-generated electron-hole pairs in TiO_2 results in low photocatalytic efficiency [6-8]. To overcome these two difficulties, many efforts have been made to modify TiO_2 nanoparticles [8-10]. One of the promising approaches is based on the metal loading. Various metals, such as Pt, Au, Pd, Rh and Ag, have been used as electron acceptors to separate the photo-induced hole/electron pair and promote interfacial charge-transfer processes [11-16].

Therefore, the aim of the present work is to study the effect of palladium on the properties and activity of the TiO_2 photocatalyst prepared by the sol-gel method. To investigate the photocatalytic efficiency of the pure and doped TiO_2, formic acid was used as a model pollutant. Formic acid is a very simple molecule which can be decomposed in simple steps leading to the increase of the pH of the treated solution.

2. Experimental Section

2.1. Synthesis details

Titanium tetrachloride (Fluka 98%) was used as a starting material. 3 gm of $TiCl_4$ was added dropwisely to 15 ml absolute ethanol under stirring. The resulting solution was stirred at room temperature to form a gel. Then, the gel was heated on the hotplate at about 80˚C to form a white powder. The powder was then dried at 110˚C for 45 minute in furnace. The dried powders were ground in an agate mortar and calcined, in air, at 350˚C, 400˚C, 480˚C, and 600˚C for 2 h in a muffle furnace. A portion of the dried precipitate was characterized by XRD and used for thermal analysis. Preparation of the Pd

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doped TiO_2 nanoparticles (Pd/TiO_2) was carried out by similar procedures used for the preparation of the undoped TiO_2 except that a calculated amount palladium chloride (required to obtain 0.05, 0.1 and 0.3 wt% of the final catalyst) was dissolved in ethanol before the addition of titanium chloride. The Pd/TiO_2 was obtained by calcinations of the obtained powder at 400˚C for under similar conditions.

2.2. Characterization

Thermogravimetric analysis (TG) and Differential Scanning Calorimetry (DSC) were performed on a Netzch STA-409EP apparatus. Thermal analyses were carried out in the range 20˚C - 1000˚C, with a heating rate of 10 $K\cdot min^{-1}$. Powdered samples (24 mg) were analyzed in alumina crucible by using α-Al_2O_3 as a reference.

X-ray diffraction spectra were recorded at room temperature using a powder diffractometer Bruker axs D8 Advance, Germany with Cu-Kα radiation source, λ = 1.5406 Å and 2Θ in the rang 10˚ - 80˚. The average crystallite size of anatase phase was determined according to the Scherrer equation. Particle size determination was carried out with a transmission electron microscope (TEM), Jeol Jem-1230. Visible-Ultraviolet spectrum was performed with a JASCO Corp., V-570 UV-V is spectrophotometer. Analysis of TiO_2 was carried out between 200 and 800 nm.

2.3. Photocatalytic Efficiency Experiments

The photocatalytic efficiency of the catalysts was investigated using a 500 ml beaker. 150 mg of pure TiO_2 or Pd/TiO_2 photocatalysts were mixed with 500 ml of formic acid solution (initial concentration of about 5 × 10^{-3} M). The resulting suspension was stirred to obtain the maximum adsorption of organic pollutant molecules on the photocatalyst surface and to make oxygen available for the reaction. After 6 h under the UV lamp and 4 h under sun light irradiation, 20 ml sample was taken for analysis. Samples were centrifuged before analysis to separate the solid particles. TOC (Phoenix 8000 Laboratory Analyzer uses sodium per-sulfate in combination with UV light to oxidize organic material) was used for the analysis of formic acid.

3. Results and Discussion

Figure 1 shows the TG and DTG curve of the undoped TiO_2. The figure presents two weight loss steps. The first step appeared between 50˚C - 380˚C. This step shows a decrease in the mass of about 14.19%. This step may be attributed to the evaporation of water and the loss of organic component and transformation of amorphous to anatase form. The second step appeared between 380˚C - 950˚C showed a decrease in mass of about 2.0%. This step may be attributed to the dehydroxylation of TiO_2 surface. The total weight loss is 16.19%. It can be concluded that a photocatalyst with a stable weight can be obtained by calcinations at about 400˚C.

Figure 2 shows the corresponding DSC curve of TiO_2 sample. There are two DSC peaks. The first peak, at around 100˚C, can be attributed to the vaporization of water and the subsequent loss of organic impurities. The second adsorption peak at ~580˚C may be attributed to the transformation of TiO_2 from anatase to rutile form [17,18].

The XRD analysis of the dried powder (that used for the preparation of the undoped TiO_2 photocatalysts before calcinations) showed amorphous material with starting of formation of the anatase phase. **Figure 3** presents the XRD results of the TiO_2 calcined at different temperatures. This figure indicates that the sample calcined at 380˚C consists of anatase phase only. Samples calcined at 480˚C and 600˚C consists of anatase

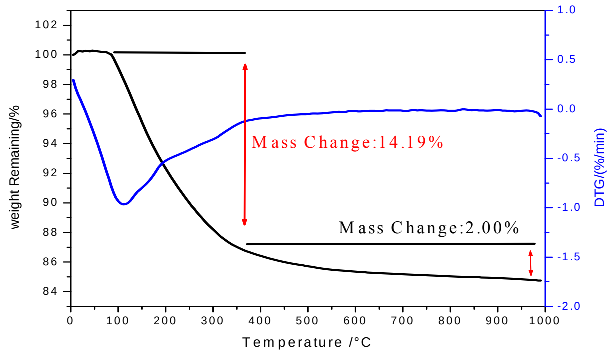

Figure 1. TG and DTG of the dried powder used for the preparation of the undoped TiO_2 nanoparticles, heating rate of 10 $K\cdot min^{-1}$ under O_2 flow.

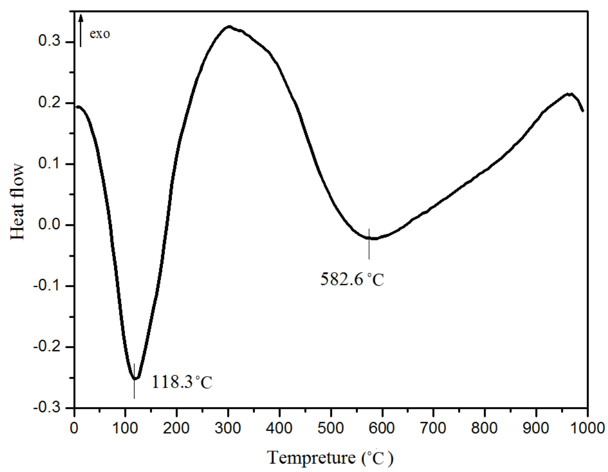

Figure 2. DSC of the dried powder used for the preparation of the undoped TiO_2 sample, heating rate of 10 $K\cdot min^{-1}$ under O_2 flow.

and rutile. **Table 1** lists the average crystallite sizes of TiO_2 (calculated from the XRD peak, according to Scherrer equation).

It can be concluded that from XRD study, anatase phase in the nano scale may be obtained by calcination of the dried powder at 380˚C and less than 480˚C.

Figure 4 shows the X-ray diffraction patterns of the undoped and 0.05%, 0.1%, and 0.3% palladium doped TiO_2 calcined at 400˚C. The XRD patterns didn't show any Pd phase (even for the 0.3% Pd doped TiO_2). This may reveal that Pd ions are uniformly dispersed in TiO_2 matrix. In the region of 2θ˚ = 10˚ - 80˚, the shape of diffraction peaks of the crystal planes of pure TiO_2 is quite similar to those of Pd/TiO_2 of different Pd concentrations.

The average crystal sizs of TiO_2 and Pd doped TiO_2 nanoparticles were calculated and also, were presented in

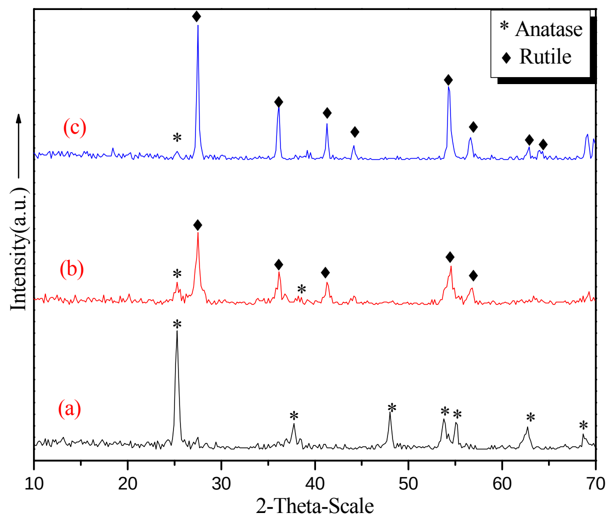

Figure 3. XRD patterns of TiO_2 nanoparticles obtained by calcinations at different temperatures (a) 380˚C, (b) 480˚C, and (c) 600˚C.

Table 1. Calculated grain size and phase composition of the doped and undoped TiO_2 catalyst at different calcination temperature from the XRD results.

Catalyst	Mean Crystallite Size (nm)	Phase %		Calcination Temperature/˚C
		Anatase	Rutile	
Undoped TiO_2	16.58	100	-	380
Undoped TiO_2	24.75	44.4	55.6	480
Undoped TiO_2	57.6	11.5	88.5	600
Undoped TiO_2	23.3	100	-	400
0.05% Pd-TiO_2	22.5	100	-	400
0.1% Pd-TiO_2	21.7	100	-	400
0.3% Pd-TiO_2	22	100	-	400

Table 1. The average crystal size was not significantly changed due to the addition of the Pd^{+2}.

Figure 5 shows the TEM result of the undoped TiO_2 nanopaeticles calcined at 480˚C. The TEM image of the undoped TiO_2 nanoparticles has a narrow size distribution (17 - 28 nm). The result of the TEM agrees with the XRD results concerning the particle size range.

The EDX (energy dispersive X-ray microanalysis) was recorded in the binding energy region of 0 - 11 keV. The result is shown in **Figure 6**. The peak from the spectrum reveals the presence of two peaks around 4.508 and 0.525 keV, respectively. The intense peak is assigned to the bulk TiO_2 and the less intense one to the surface TiO_2. The peaks of Pd are distinct in **Figure 7** at 2.8 and 3.6 keV. This result confirms the existence of Pd atoms in the TiO_2 matrix.

The UV-visible spectra of the undoped TiO_2 and Pd doped TiO_2 samples prepared by calcinations at 400˚C are shown in **Figure 7**. The onset wavelength of absorption used to calculate the optical band gap was determined by extrapolation of the base line and the absorption edge. **Table 2** shows the calculated absorption onset (λ) and the corresponding band gap (Eg) for doped

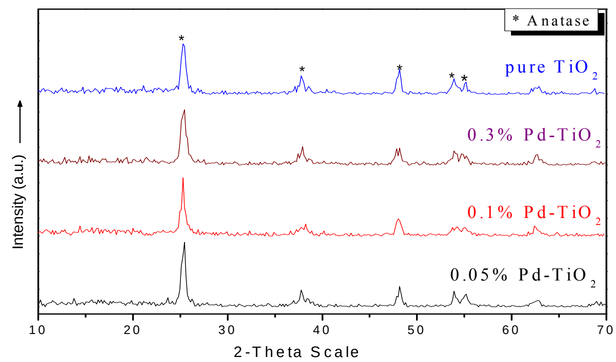

Figure 4. XRD patterns of the doped and undoped TiO_2 nanoparticles calcined at 400˚C.

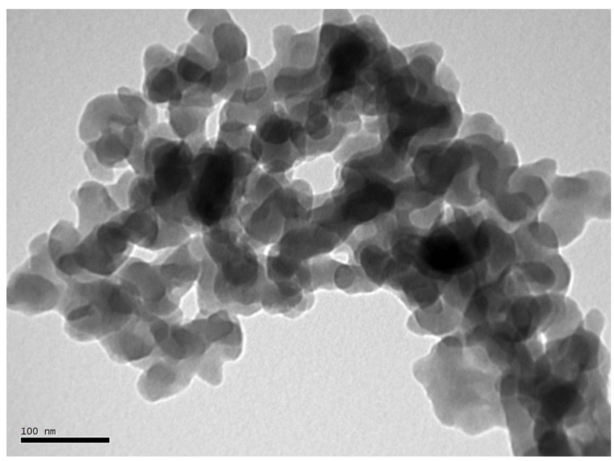

Figure 5. TEM image of TiO_2 nanoparticles prepared by calcinations at 480˚C.

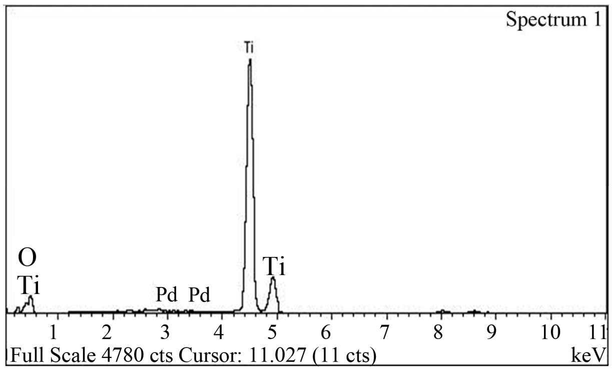

Figure 6. EDX pattern of 0.03% Pd doped TiO_2 nanoparticles.

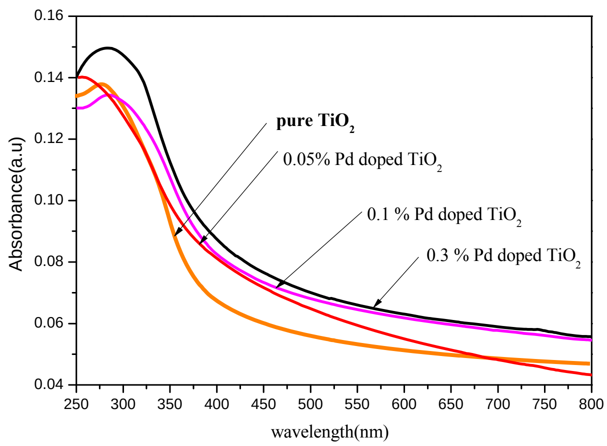

Figure 7. UV-Vis absorption spectra for undoped and Pd doped TiO_2 nanoparticles prepared by calcinations at 400˚C.

Table 2. Absorption band edge (λ) and band gap (Eg) of undoped and Pd doped TiO_2 samples.

Photocatalyst	Absorption Band Edge (λ), nm	Band Gap (Eg), eV
Pure TiO_2	365.85	3.39
0.05% Pd Doped TiO_2	369.9	3.35
0.1% Pd Doped TiO_2	375.36	3.29
0.3% Pd Doped TiO_2	404.93	3.06

and undoped TiO_2.

The absorption spectrum of Pd doped TiO_2 consists of a single broad intense absorption at the range 365.85 - 404.93 nm can be attributed to the charge-transfer from the valence band to the conduction band [11]. The undoped TiO_2 showed absorbance in the shorter wavelength region. The UV-Vis absorption results showed a red shift of the absorption onset value due to modification of TiO_2 with Pd of different concentrations as shown in **Figure 7**. It is known that doping of various transitional metal ions into TiO_2 could shift its optical absorption edge from UV into visible light range [19].

3.1. Photocatalytic Efficiency (Removal of Formic Acid)

Formic acid is a simple molecule that can be mineralized in simple steps leading to the increase of the pH of the treated solution. One possible route for formic acid removal may be initiated through the direct transfer of an electron from the adsorbed formic acid to the surface positive hole of the photocatalyst [20]. Also, it is well known that hydroxyl radicals are produced in photocatalytic reactions illuminated by radiation of suitable wave length. These hydroxyl radical may react with the HCOO-molecule to form water and ·COO-, which can be further decomposed through the reaction with oxygen [20]. Presence of palladium can modify the photocatalytic effect through increasing the life time of charge separation and shifting the absorbance to longer wave length.

Formic acid concentration was measured by the Total Organic Carbon (TOC). TOC was decreased from 52.2 mg/l to 35 mg/l using the 0.05% Pd doped TiO_2 under UV irradiation, **Figure 8**. For the undoped TiO_2 photocatalyst, the TOC was decreased to 23.6 mg/L. The pH of the solution also was changed from 3.06 to 3.17 and 3.3 for doped and undoped TiO_2 photocatalysts, respectively within the same time (see **Table 3**). The change of the pH was taken as a signal for the removal of formic acid. It can be seen that under UV irradiation, the undoped TiO_2 exhibits better efficiency than the Pd/TiO_2 photocatalyst.

Removal of formic acid by pure TiO_2 and Pd/TiO_2 were examined using sun light as a radiation source **Figure 9**. It can be seen that Pd/TiO_2 shows higher efficiency than the pure TiO_2. Also, it can be seen that there is a gradual increase in the efficiency of the Pd/TiO_2 with increasing palladium content in the catalyst. TOC was decreased from 61 mg/L to 49.6, 34.2, 2.19 and

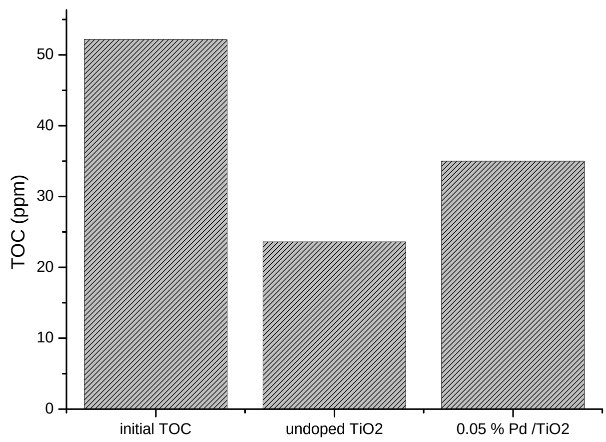

Figure 8. Removal of formic acid by undoped TiO_2 and 0.05% Pd doped TiO_2 under UV irradiation. Catalyst wt. 150 mg and λ = length 360 nm.

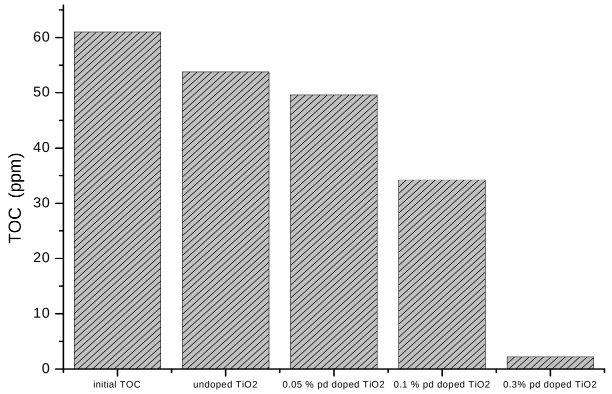

Figure 9. Removal of formic acid by the undoped TiO_2, 0.05%, 0.1% and 0.3% Pd/TiO_2. Catalyst wt 150 mg under sun light irradiation.

Table 3. TOC and pH values for formic acid solution treated by doped and undoped TiO_2 nanoparticles prepared by calcinations at 400˚C under UV irradiation for 6 hrs.

Sample Name	pH	TOC	Degradation Rate (%)
Formic acid Solution	3.06	52.2	-
Undoped TiO_2	3.3	23.6	54.8
0.05% Pd Doped TiO_2	3.17	35	33

Table 4. TOC results for doped and undoped TiO_2 nanoparticles annealed at 400˚C under sun light irradiation for 4 hrs.

Sample Name	pH	TOC	Degradation Rate (%)
Formic Acid Solution	2.98	61	-
Undoped TiO_2	2.99	53.8	11.8
0.05% Pd Doped TiO_2	3.08	49.6	18.69
0.1% Pd Doped TiO_2	3.02	34.2	43.93
0.3% Pd Doped TiO_2	3.58	2.19	96.4

53.8 mg/L for 0.05%, 0.1%, 0.3% Pd doped TiO_2 and undoped TiO_2, respectively under sun light irradiation within the same time (see **Table 4**). The pH of the solution also was changed from 2.98 to 3.08, 3.02, 3.58 and 2.98 for 0.05%, 0.1%, and 0.3% Pd doped TiO_2 and undoped TiO_2 photocatalysts, respectively, within the same time.

4. Conclusion

The pure and palladium doped TiO_2 (Pd/TiO_2) nanoparticles were prepared by the sol gel method. Samples prepared by calcinations at 380˚C contain anatase phase only. A mixture of anatase and rutile was obtained at higher calcination temperatures. Doping TiO_2 with palladium in the concentration range of 0.05 to 0.3 has no significant effect on the particle sizes and did not result in the formation of a new crystalline phase. It was confirmed that the incorporation of Pd in TiO_2 matrix shifts the onset wave length of absorption to higher values (red shift). Under UV irradiation, the pure TiO_2 exhibited higher efficiency than the palladium doped TiO_2 for formic acid removal from water. However, when sun light was used as the radiation source, the palladium doped photocatalyst exhibited higher efficiency than the pure TiO_2 and the photocatalytic efficiency increases with increasing palladium content up to a concentration of 0.3% (0.3% Pd/TiO_2).

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