



## Synthesis and photoactivity of Pd substituted nano-TiO<sub>2</sub>

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### ABSTRACT

Palladium substituted and palladium impregnated nanocrystalline anatase titania were prepared by solution combustion method. These catalysts were characterized by XRD, XPS, FT-IR, TGA, BET, UV-vis absorption, TEM and photoluminescence (PL) measurements. The catalysts have been used for the first time for liquid phase photocatalysis. The photocatalytic degradation of various dyes such as Alizarin Red S, Methylene Blue, Orange G and Rhodamine B and phenol and 4-chlorophenol was investigated under UV exposure. Though Pd-ion substituted titania has significantly higher photocatalytic activity compared to unsubstituted titania for NO reduction and NO decomposition, the initial rate of degradation for all the dyes, phenol and 4-chlorophenol was lesser in Pd substituted and impregnated titania compared to that of unsubstituted titania. This reduced reaction rate was attributed to a decrease in the surface area and PL intensity. This study shows that the photoluminescence is the key factor in determining the photocatalytic activity in liquid phase reactions.

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### 1. Introduction

Semiconductor photocatalysis is an emerging area for the effective detoxification of noxious organic water pollutants [1–3]. Photocatalytic degradation results in the demineralization of organic matter into carbon dioxide, water and mineral acids. Although many photocatalysts have been investigated [4] in the past, anatase phase TiO<sub>2</sub> remains the photocatalyst of choice, due to its high photoactivity, low cost and easy synthesis.

Previous studies [5,6] indicate that titania synthesized by solution combustion technique shows superior photocatalytic activity compared to the commercial Degussa P-25 (DP-25) titania. The effect of doping various transition metal ions such as Cu<sup>2+</sup>, Fe<sup>3+</sup>, Ce<sup>4+</sup>, Zr<sup>4+</sup>, V<sup>5+</sup> and W<sup>6+</sup> into combustion synthesized titania has been examined [6]. Though the metal ion doped titania showed an increased photocatalytic activity than the commercial DP-25 TiO<sub>2</sub> catalyst, the catalytic activity was lower than that of the unsubstituted TiO<sub>2</sub>. According to the proposed mechanism, the recombination of photogenerated electrons and holes [1,4] is inhibited as the metal scavenges the electrons. This also aids in the generation of hydroxyl radical (\*OH), capable of oxidizing organic matter. Other than metal ion substitution, metal ions can also be impregnated on the titania matrix. Metals can also participate with the titania photocatalyst by simply being present on the surface of the TiO<sub>2</sub> matrix, thereby preventing the charge-

carrier recombination. While some studies report that the metal ion substituted/impregnated catalysts enhance the photocatalytic degradation rate [7–12], others report a reduction in rate [5,6], thus indicating an optimal metal concentration for high activity. Dyes are an important class of organic water pollutants and, therefore, many studies have been conducted on the photodegradation of dyes and other organic pollutants like phenols, substituted phenols and their mixtures [13–16].

Solution combustion technique has been extensively used for the synthesis of nano-titania [5,6,17] and ZnO nanopowders [18]. Recently, we have shown that Pd-ion substituted titania (Ti<sub>0.99</sub>Pd<sub>0.01</sub>O<sub>2-δ</sub>) has significantly higher photocatalytic activity compared to unsubstituted titania for NO reduction and NO decomposition [19]. In this work, we have explored the liquid phase catalytic properties of this catalyst by examining the degradation of anthraquinonic (Alizarin Red S), heteropolyaromatic (Methylene Blue), xanthene (Rhodamine B) and azoic (Orange G) dyes, and organic pollutants such as phenol and 4-chlorophenol.

### 2. Experimental

#### 2.1. Catalyst preparation

Nanosize anatase titania was prepared by the solution combustion synthesis methodology. This method involves the combustion of aqueous solutions containing stoichiometric amounts of precursor compound, titanyl nitrate (TiO(NO<sub>3</sub>)<sub>2</sub>) and fuel, glycine (H<sub>2</sub>N-CH<sub>2</sub>-COOH). Titanyl nitrate was synthesized by the reaction of titanyl hydroxide [TiO(OH)<sub>2</sub>] obtained by the controlled

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hydrolysis of titanium isopropoxide  $[\text{Ti}(\text{i-OPr})_4]$  with nitric acid. The details of the synthesis are reported elsewhere [5]. The combustion mixture for the preparation of 1 at.% Pd/TiO<sub>2</sub> contained titanium nitrate, palladium chloride (PdCl<sub>2</sub>) and glycine in the molar ratio 0.99:0.01:1.14. 1 at.% Pd impregnated TiO<sub>2</sub> was prepared by adding calculated amount of PdCl<sub>2</sub> drop wise to an aqueous suspension (100 mL) of combustion synthesized TiO<sub>2</sub> in presence of reducing agent, hydrazine hydrate, under magnetic stirring at room temperature. The suspension was stirred for 30 min. The sample was washed with distilled water till all the chloride ions were completely removed and dried at 120 °C for 24 h.

## 2.2. Catalyst characterization

The catalysts Pd substituted TiO<sub>2</sub> (Pd/TiO<sub>2</sub>(sub)), Pd impregnated TiO<sub>2</sub> (Pd/TiO<sub>2</sub>(imp)), unsubstituted combustion synthesized TiO<sub>2</sub> (CS TiO<sub>2</sub>) and commercial DP-25 TiO<sub>2</sub> were characterized by various techniques. The X-ray diffraction (XRD) patterns were recorded on a Philips X'pert Pro Diffractometer with Cu K $\alpha$  radiation in the  $2\theta$  range from 20° to 80° at a scanning rate of 1°/min. The X-ray photoelectron spectra (XPS) were recorded with ESCA-3 Mark II spectrometer (VG Scientific Ltd., UK) using Al K $\alpha$  radiation (1486.6 eV). Fourier transform-infrared (FT-IR) studies were carried out with Perkin-Elmer (FT-IR-Spectrum-1000) spectrometer in the transmission mode. Thermo-gravimetric analysis (TGA) was carried out with a thermal analyzer (Perkin-Elmer, Pyris Diamond) to determine the adsorbed water. UV-vis absorption spectra were obtained using Perkin-Elmer UV-visible spectrophotometer. Every sample was dry pressed into a 10 mm diameter round disk containing about 150 mg of catalyst. Absorption spectra were referenced to BaSO<sub>4</sub>. Transmission electron microscopy (TEM) of 1 at.% Pd/TiO<sub>2</sub>(sub) and 1 at.% Pd/TiO<sub>2</sub>(imp) was carried out using JEOL JEM-200CX operated at 200 kV. The photoluminescence (PL) measurements were performed in a luminescence spectrophotometer (Perkin-Elmer 55) operated at room temperature.

## 2.3. Photoreactor

The photocatalytic activity of 1 at.% Pd/TiO<sub>2</sub>(sub) and 1 at.% Pd/TiO<sub>2</sub>(imp) was evaluated by measuring the degradation rates under UV exposure. The activity of the catalyst was compared with CS TiO<sub>2</sub> and DP-25 TiO<sub>2</sub>. The photochemical reactor employed in the present study consisted of a jacketed quartz tube of 3.4 cm i.d., 4 cm o.d., and 21 cm length. A high-pressure mercury vapor lamp of 125 W (Philips, India) that radiated predominantly at 365 nm (3.4 eV) was placed inside the reactor after carefully removing the outer shell. Water was circulated through the annulus to avoid heating during the reaction. Further details are provided elsewhere [5].

The catalyst concentration employed in the current study was 1 g L<sup>-1</sup> for all the catalysts and all the experiments were performed in the natural pH of the dye. The initial concentration employed for the dye solutions range from 10 mg L<sup>-1</sup> to 100 mg L<sup>-1</sup>.

## 2.4. Sample analysis

Before analyzing the degraded samples of all the dyes and phenols, the samples were filtered using Millipore membrane filters and centrifuged to remove the catalyst particles prior to analysis. For the analysis of dyes, the centrifuged sample was used to record the UV-vis spectra (Systronics, Spectrophotometer-166) in the wavelength range 200–800 nm. The characteristic wavelength,  $\lambda_{\text{max}}$  values are 420 nm, 664 nm, 475 nm and 553.6 nm for Alizarin Red S (ARS), Methylene Blue (MB), Orange G (OG)

and Rhodamine B (RB), respectively. For all the dyes, calibration based on Beer-Lambert law was used to quantify the concentration.

Several intermediates are formed during the degradation of phenols [14,15]. To quantify these intermediates, the samples were analyzed in HPLC. The HPLC consisted of an isocratic pump (Waters 501), Rheodyne injector (model 7010, sample loop-50  $\mu\text{L}$ ), C-18 column, UV detector (Waters 2487) and a data acquisition system. The eluent stream consisted of 90:10 (v/v) water:methanol pumped at 0.5 mL/min for analyzing phenol and 4-chlorophenol. The UV absorbance detector was set at 270 nm and 280 nm for phenol and 4-chlorophenol, respectively. The chromatographic areas were converted to concentration values using the calibration curves based on pure compounds. The compounds were identified and the concentrations were further verified by LC-MS (Waters 3100 Mass Detector).

Many of the experiments were repeated in triplicate and the error in the determination of the concentration was  $\pm 1 \text{ mg L}^{-1}$ . Experiments were conducted in aqueous solutions with pH varying from 2 to 11. The XRD pattern before and after the experiment showed no change indicating that the material is stable and no metal was leaching out from the catalyst into solution.

## 3. Results and discussion

### 3.1. Catalyst characterization

The XRD patterns of 1 at.% Pd/TiO<sub>2</sub>(sub) and 1 at.% Pd/TiO<sub>2</sub>(imp) are shown in Fig. S1 1 (see supplementary data). The pattern can be indexed to TiO<sub>2</sub> in the anatase phase only. The rutile and brookite phases were not observed. The crystallite size is determined from the (1 0 1) peak in the XRD pattern using the Scherrer formula, and the average size of both Pd substituted and impregnated titania crystallites were 8–10 nm. Rietveld refinements of the diffraction patterns of Ti<sub>0.99</sub>Pd<sub>0.01</sub>O<sub>2- $\delta$</sub> , 1 at.% Pd/TiO<sub>2</sub>(imp) were carried out using the FullProf-98 program, and a good agreement between calculated and observed pattern was obtained. The flat background indicates that the Pd substituted titania is crystalline in nature. The change in lattice parameters,  $R_{\text{bragg}}$  and  $R_{\text{f}}$  with respect to combustion synthesized TiO<sub>2</sub> are listed in Table S1 (see supplementary data).

Pd metal peaks (1 1 1) were not found in the XRD patterns of 1% Pd/TiO<sub>2</sub>(sub). However, for 3% Pd/TiO<sub>2</sub>, rutile phase goes up to 30% and Pd (1 1 1) peaks appear [19]. The diffraction lines due to PdO were also not present in 1% Pd/TiO<sub>2</sub>(sub). However, 1% Pd/TiO<sub>2</sub>(imp) indeed shows Pd (1 1 1) peaks. The absence of Pd (1 1 1) peak and diffraction lines due to PdO in the combustion synthesized sample of 1% Pd/TiO<sub>2</sub> suggests the formation of Ti<sub>0.99</sub>Pd<sub>0.01</sub>O<sub>1.99</sub>. Further, the Rietveld refinement of 1% Pd/TiO<sub>2</sub>(sub) has been carried out and the difference plot does not show detectable peaks due to Pd or PdO [19].

The Pd(3d<sub>5/2,3/2</sub>) core level spectra of Pd metal powder, 1% Pd/TiO<sub>2</sub>(imp), PdO and 1% Pd/TiO<sub>2</sub>(sub) are presented in Fig. S1 2. Pd(3d<sub>5/2,3/2</sub>) peaks at 335 eV and 340.5 eV indicate that Pd metal is in zero valent state. In the Pd impregnated TiO<sub>2</sub> also, binding energy of Pd(3d<sub>5/2,3/2</sub>) peaks are at 335 eV and 340.5 eV. Pd(3d<sub>5/2,3/2</sub>) peaks at 336.8 eV and 342.2 eV in the PdO sample shows that Pd is in 2+ state. In the combustion synthesized Pd/TiO<sub>2</sub>(sub), Pd(3d<sub>5/2</sub>) core level binding energy is at 337.2 eV. Thus the binding energy of Pd ions in TiO<sub>2</sub> is higher than Pd<sup>2+</sup> in PdO. Thus, Pd in the combustion synthesized TiO<sub>2</sub> is in 2+ state and PdO diffraction lines are absent in the XRD. Further, based on XPS data and the peak intensities [19], the surface concentration of Pd<sup>2+</sup> ion in 1 at.% Pd/TiO<sub>2</sub>(sub) is 2.3% as against 9.4% in the Pd metal impregnated on TiO<sub>2</sub>. Thus, Pd ion is indeed substituted in TiO<sub>2</sub> crystallites.

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