

## CO-DOPING EFFECT OF CARBON AND YTTRIUM ON PHOTOCATALYTIC ACTIVITY OF TiO<sub>2</sub> NANOPARTICLES FOR METHYL ORANGE DEGRADATION

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Nanoparticles of titanium dioxide (TiO<sub>2</sub>), co-doped with carbon (C) and yttrium (Y) were prepared by hydrothermal method using titanium tetraisopropoxide (TTIP), glucose and Y<sub>2</sub>O<sub>3</sub> as precursors. The prepared samples calcined at 500<sup>o</sup>C were characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and UV-Vis diffuse reflectance spectroscopy (DRS). XRD results showed anatase phase of TiO<sub>2</sub> nanoparticles and crystallite size of TiO<sub>2</sub> nanoparticles were decreased with doping of C and Y. The decrease of particle size was also confirmed by TEM. FTIR measurements demonstrate the identification of functional groups present at the surface of TiO<sub>2</sub>. Absorption spectra showed a red shift of absorption band edge in visible light region due to synergistic effects of Y and C. The photocatalytic activity measurements were performed for the degradation of methyl orange (MO) dye under visible light illumination. The results obtained demonstrated that photocatalytic activity was enhanced due to doping and codoping of C and Y. It is expected that this work will give new insights in the developments of novel visible light active photocatalysts for environmental issues.

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### 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) semiconductor is the subject of huge amount of studies related to air cleaning and water purification [1–9]. TiO<sub>2</sub> is the most suitable photocatalyst for water treatment and recovery due to its high photocatalytic activity, good chemical and biological stability, high energy efficiency, relatively low cost and non-toxicity [10]. Photocatalysis by titanium dioxide has become an extremely promising technology for environmental purification, owing to a number of advantages over conventional processes [11,12]. However, the applications of TiO<sub>2</sub> are limited due to the fast recombination of electron-hole pairs and its wide band gap, which absorbs only ultra-violet light [13]. Therefore, the study of modifying TiO<sub>2</sub> in order to reduce the electron-hole pairs recombination and sensitization towards visible light is one of the most challenging topics in photocatalysis research. Previously, several strategies including the doping of TiO<sub>2</sub> with metals and non metals have been adopted [14]. In some reports, non-metal doping such as B, C, N, F and S has been proposed to favor the electron-hole separation and enhance the visible light absorption property [17-20]. Moreover, it was also found effective with doping of rare earth metals including Pr, Eu, Ce, Y, Er, Gd, La, Nd and Sm which efficiently reduced the recombination of electrons-hole pairs in TiO<sub>2</sub> photocatalysis [21-24]. Therefore, it will

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be good strategy to co-dope TiO<sub>2</sub> with metal and non metal for the enhancement of photocatalytic activity.

In present work TiO<sub>2</sub> co-doped with Y and C was prepared by hydrothermal method and samples were characterized by different techniques. The photocatalytic performance was evaluated through the degradation of methyl orange under visible light irradiation. The possible mechanism for the photocatalysis was also discussed.

## 2. Synthesis and characterization of TiO<sub>2</sub> nanopowders

Pure TiO<sub>2</sub> and co-doped TiO<sub>2</sub> nanoparticles have been prepared by hydrothermal method using titanium tetraisopropoxide (TTIP, 98%) as precursor material. TTIP was diluted with isopropanol in the molar ratio of 01:10. After 15 min stirring 10 ml of deionized water was added drop wise and solution was put into an autoclave at 150 °C for 20h then this solution was dried at 120 °C. Same procedure was also adopted for carbon and yttrium doping using Y<sub>2</sub>O<sub>5</sub> and C<sub>6</sub>H<sub>12</sub>O<sub>6</sub> as source materials. Finally, all the samples were calcined at 500 °C for characterization.

Powder X-ray diffraction (XRD) patterns were collected from 10<sup>0</sup> to 80<sup>0</sup> in 2 $\theta$  with 0.02<sup>0</sup> steps/s using a Rigaku D/max-3B X-ray diffractometer with Cu K $\alpha$  as radiation source ( $\lambda=0.15406$  nm) at 40 kV and 36 mA. Transmission electron spectroscopy (TEM) study was carried out on a JEOL JEM-1200EX electron microscope instrument operated at 200 kV. Fourier transform infrared spectrophotometer (FTIR, Perkin-Elmer System 2000) was used to determine the specific functional groups. UV-vis diffuse reflectance spectra (DRS) were measured in the range of 300-800 nm using a HITACHI U-4100 UV-vis spectrometer with an integrating sphere accessory. Their reflectance was converted to absorbance by Kubelka-Munk function:  $F(R) \propto K/S = (1 - R)^2/2R$ , where K is the absorption coefficient, S is the scattering coefficient, and R is the diffuse reflectance.

The photocatalytic activity of different samples were estimated by monitoring the degradation of methyl orange (MO) in a self-assembled apparatus with a metal halogen lamp (HQBT, 400 W/D, OSRAM, Germany) as the radiation source. The visible-light ( $\lambda \geq 420$  nm) used in the present study was obtained by the filter with cut-off wavelength of 420 nm. Typically, for the photocatalytic experiment, 100 mg photocatalysts were suspended in 100 mL MO aqueous solution with a concentration of 10 mg L<sup>-1</sup> in a beaker. The suspension was magnetically stirred for 30 min to reach the adsorption/desorption equilibration without visible light exposure. Following this, the photocatalytic reaction was started by the exposure of visible light. After a setup exposure time, 5 ml suspension was sampled, centrifuged, and the supernatant was taken out for UV-vis absorption spectrum. The intensity of the main absorption peak (464 nm) of the MO dye was referred to as a measure of the residual MO dye concentration (C).

## 3. Results and discussion

Fig. 1 displays the XRD results for the samples calcined at 500°C. The characteristic diffraction peaks at 25.4°, 38.1°, 48°, 54.8°, 62.8°, 71.1° and 74.9° corresponds to hkl values (101), (004), (200), (105), (204), (220) and (215) showed that all samples have anatase structure and no rutile or brookite phase being present in the samples. The characteristic peaks for carbon and yttrium elements are also not present due to small addition of doping content. It may be due to the reason that most of the carbon and yttrium possibly covered the surface and may be acted as a photosensitizer [25,26]. Moreover, it can be seen that the intensity of peaks was decreased after doping and co-doping with carbon and yttrium, which clearly show the presence of doping influence on TiO<sub>2</sub>. The crystallite size of the samples were calculated from full-width at half-maxima of the (101) peak of the anatase TiO<sub>2</sub> by Debye-Sherrer equation [27]. The average crystallite size calculated from above equation for pure TiO<sub>2</sub> was 9.5 nm and for C/TiO<sub>2</sub>, Y/TiO<sub>2</sub> and C/Y/TiO<sub>2</sub> samples are 8.8 nm, 7.7 nm and 6.9 nm respectively. These results show that doping and co-doping can inhibit the growth of TiO<sub>2</sub> crystallites [27]. It was reported that photocatalytic

activity of catalyst with smaller crystallite size is better than those of larger size particles [28]. So, it is expected that it would be efficient catalyst during the degradation process.

Fig. 2 shows the TEM images of the C/Y/ TiO<sub>2</sub> nanoparticles. It can be seen that TEM images show a large number of small particles. The average particle size estimated from TEM image for this sample is in the range of 10-15 nm which is consistent with the crystallite size estimated using Scherer equation from XRD results.

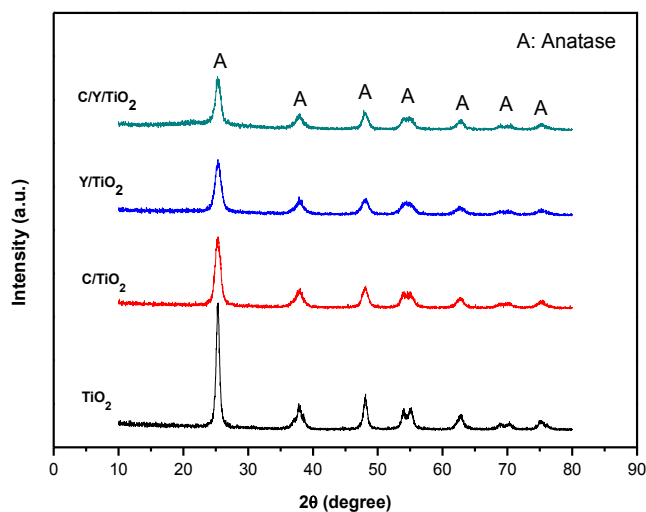


Fig. 1 XRD patterns for samples calcined at 500 °C.

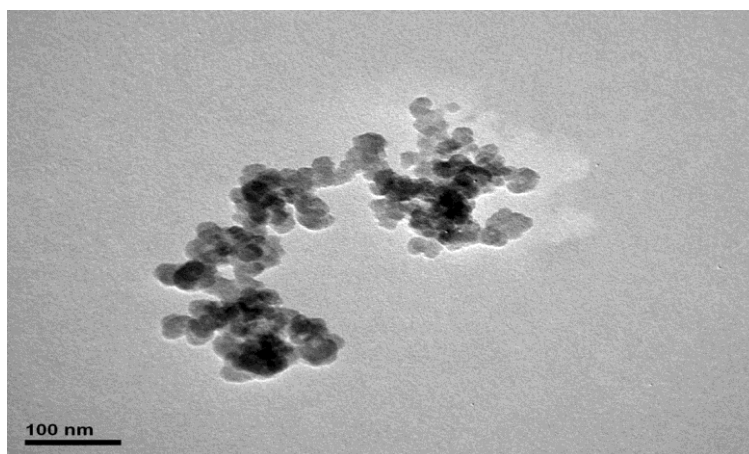


Fig. 2 TEM image of C/Y/TiO<sub>2</sub> nanoparticles calcined at 500 °C.

FTIR measurements for pure TiO<sub>2</sub> and co-doped samples were carried out in the range of 4000–400 cm<sup>-1</sup> to identify the functional groups adsorbed on TiO<sub>2</sub> surface as shown in Fig. 3. The spectra exhibited an absorption peak at about 1640 cm<sup>-1</sup> associated with bending vibration of free water molecule and peaks at 3444cm<sup>-1</sup> corresponds to bending vibration of O–H bond and stretching vibration of hydroxyl or adsorbed water molecule that may be beneficial in promoting the photocatalytic reaction since these can react with photogenerated holes on catalyst surface to produce hydroxyl radicals a powerful oxidant [29]. A band between 1300 cm<sup>-1</sup>–1500 cm<sup>-1</sup> indicates the presence of asymmetrical vibration of carboxyl group C–H bond [30]. The band in region 2800 cm<sup>-1</sup>–3000 cm<sup>-1</sup> centered around 2930 cm<sup>-1</sup> in co-doped catalysts corresponds to asymmetrical stretching vibration of –CH and –CH<sub>2</sub> group that shows the presence of carbonaceous species [31]. Absorption band at 582 cm<sup>-1</sup> indicates Ti–O stretching vibration and O–Ti–O bending vibration of crystalline titania anatase phase.

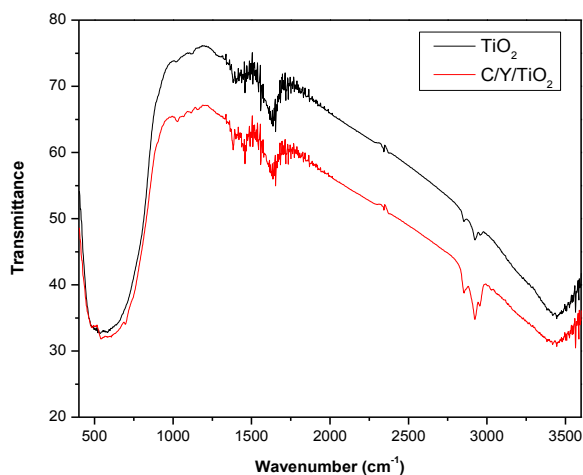


Fig. 3 FTIR spectra of pure and C-Y-TiO<sub>2</sub> samples.

UV-Vis diffuse reflectance spectra were taken for pure, single doped and co-doped TiO<sub>2</sub> nanopowders. The absorption edges of TiO<sub>2</sub>, C/TiO<sub>2</sub>, Y/TiO<sub>2</sub>, C/Y/TiO<sub>2</sub> were observed at 386 nm, 390 nm, 398 nm and 405 nm respectively. It is obvious that the doping of carbon and yttrium has significant effect on visible light absorption [32]. Therefore, a noticeable shift of absorption edge to the visible light region was observed for doped and co-doped TiO<sub>2</sub> samples.

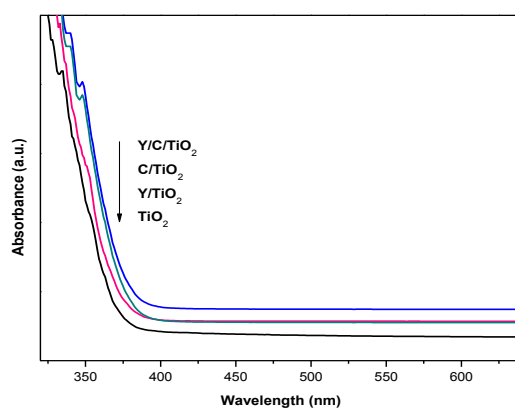


Fig. 4 Absorption spectra of different samples calcined at 500 °C.

Fig. 5 show the results of photocatalytic decomposition of methyl orange (MO) dye using different photocatalysts under visible light irradiation. It is obvious that C/TiO<sub>2</sub> showed greater photocatalytic activity than pure and Y/TiO<sub>2</sub> nanopowders. Doping of yttrium also causes an increase in photocatalytic efficiency as compared to undoped TiO<sub>2</sub>. The highest photocatalytic performance was observed for co-doped C/Y/TiO<sub>2</sub> sample. The increase in photocatalytic activity of doped and co-doped samples can be attributed to smaller crystallite size and enhanced visible light absorption [33,34].

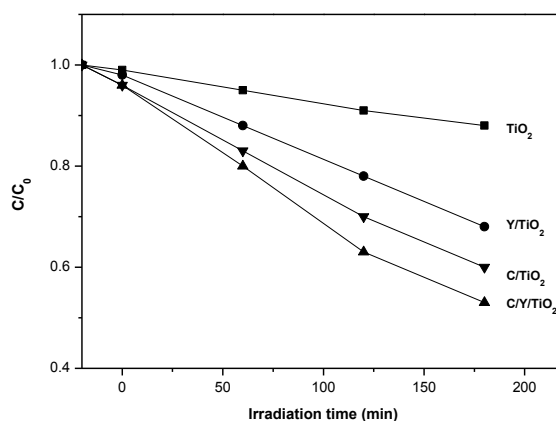


Fig. 5 Photocatalytic activity different samples for methyl orange degradation under visible light irradiation ( $\lambda \geq 420$  nm).

#### 4. Conclusion

Carbon and yttrium co-doped TiO<sub>2</sub> photocatalysts were prepared by hydrothermal method for the degradation of methyl orange (MO) dye. XRD results showed decrease in crystallite size due to doping and co-doping. FTIR spectra showed different functional groups attached to TiO<sub>2</sub> during synthesis process. All doped and co-doped samples exhibited higher photocatalytic performance under visible light irradiation. Maximum photocatalytic activity was observed for C/Y/TiO<sub>2</sub> catalyst due to the synergistic effects of smaller crystallite size and wider spectral response in visible light region.

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