



# Study of synergistic effect of Sc and C co-doping on the enhancement of visible light photo-catalytic activity of TiO<sub>2</sub>



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## ABSTRACT

Scandium and carbon co-doped TiO<sub>2</sub> catalyst was prepared through a simple sol-gel synthesis method by using scandium nitrate as scandium dopant precursor, glucose as carbon precursor and tetrabutyl orthotitanate as titanium precursor and calcined them at 450 °C for 3 h. The characterizations of the prepared samples were accomplished through X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-visible diffuse reflectance spectroscopy (UV-Vis DRS), photoluminescence spectroscopy (PL), Fourier transformation infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and Brunauer-Emmett-Teller (BET). The X-ray diffraction results of the samples showed the decrease in the crystal size of the sample with the subsequent increase in the specific surface area as shown by Brunauer-Emmett-Teller. The UV-visible diffuse reflectance spectroscopy displayed the blue shift in the absorption together with the photoluminescence spectroscopy revealed the decrease in the recombination of electrons and holes by the addition of the scandium and then after the certain optimum value, the further increase of the scandium further increased the recombination of electrons and holes. The photo-catalytic activity of the samples was investigated with the help of photo-catalytic degradation of Acid orange 7 under visible light irradiation. The degradation of Acid orange 7 was highly increased for the Sc and C co-doped samples compared to the single C doped sample. And the sample 0.2 Sc/C-TiO<sub>2</sub> had the maximum increase. The enhanced photo-catalytic performance was due the decrease of the crystal size, increase of the surface area, increase in the surface hydroxyl groups, and increase of the lifetime of the electrons and holes because of the synergistic effect of the Sc and C co-doping in TiO<sub>2</sub>.

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## 1. Introduction

The development of photo-catalysis for the degradation of the pollutants is a matter of growing interest from the last three decades. A large number of different semiconductor photo-catalysts have been employed so far for the degradation of the different organic pollutants, however TiO<sub>2</sub> catches much more attention than any of other photo-catalyst because of the certain advantages associated with it. TiO<sub>2</sub> is an ideal photo-catalyst of its kind due to its good chemical stability, non-toxicity, low cost, easy availability and high photo-catalytic activity. However, the performance of the TiO<sub>2</sub> catalyst is hindered by certain discrepancies. One

of the drawbacks which hinder its photo-activity is its large band gap (3.2 eV), which make it can only be activated under the UV light that comprises only 4–5% of the solar light and leaving the rest ineffective for the photo-catalysis. The other shortcoming of the TiO<sub>2</sub> catalyst is the fast recombination of photo-generated electrons and holes produced on its surface.

Significant counts of attempts [1–5] have been made to reduce the effect of the above mentioned subjects and to make it easily available for the photo-catalysis under the visible light irradiation. Most considerable methods adopted for the enhancement of its visible light response towards the degradation of the dyes were their doping with the metal and non-metal [6–10]. The metal doping has been proved very useful in the enhancement of the catalyst performance under the visible light because the metal doping introduces mid-level states which reduces the band gap and makes possible for the photo-generated electron to transfer to the conduction band [11], also metal doping has been

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proved to be very helpful to increase the lifetime of the electrons and holes [12]. Considerable numbers of reports have been published for the enhancement of the visible light photo-activity with the help of metal doping. For example, Jiefang Zhu et al. [13] prepared the Fe doped  $\text{TiO}_2$  by using hydrothermal method and successfully improved the photo-catalytic activity for the dye XRG under the visible light due the narrowing of the band gap and reduction of the recombination of electrons and holes. Similarly, Shamaila Sajjad et al. [14] degraded phenol and chromium under the visible light irradiation by the doping of Bi in the  $\text{TiO}_2$  due to the narrowing of the band gap and suppression to the recombination of electrons and holes. Non-metal doping has also been proved to be very favorable for reduction of the band gap of  $\text{TiO}_2$  and enhancement of the visible light response. Mingyang Xing et al. [15] prepared the nitrogen doped  $\text{TiO}_2$  by adjusting a pH range using the ammonium nitrate and ammonia water as the nitrogen source and efficiently degraded 2, 4-DCP under the visible light due the narrowing of band gap. Likewise, Xiaona Lu et al. [16] reported the synthesis of boron doped  $\text{TiO}_2$  by the aid of low temperature autoclave sol method and attributed the high visible light photo-catalytic activity of the samples to the reduction of the band gap and increase of the surface area.

Inspired by the positive effects of the metals and non-metals doping, many research groups tried the co-doping technique with  $\text{TiO}_2$  by different metal–metal couples [17,18], non-metal–non-metal couples [19–21] and metal–non-metal couples [22–25]. The co-doped samples demonstrated much better visible light photo-catalytic activities as compared to the single doped  $\text{TiO}_2$ , due the synergistic effects of the both dopants.

In the recent research work we prepared a novel Sc and C co-doped  $\text{TiO}_2$  photo-catalyst through simple sol–gel method. The characterizations of the prepared catalysts were carried out with the help of XRD, XPS, BET, TEM, HR-TEM, UV–Vis. DRS, PLS, FTIR etc. The photo-catalytic activities of the samples were evaluated by the degradation of the aqueous solution of AO7 and the results demonstrated that our co-doped samples have significantly enhanced photo-catalytic degradation of the dye under visible light irradiation, which is discussed in detail in the article.

## 2. Materials and method

### 2.1. Materials used

All the major reagents employed in the synthesis were AR grade and used without further purification. Scandium nitrate was used as a scandium doping source and ethanol as the solvent. They both were purchased from Sinopharm Chemical Reagent Co., Ltd. Titanium tetrabutoxide (TBOT) was used as titanium while glucose as carbon doping source. Both of these chemicals were purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. Acid Orange 7 (AO7) was purchased from Acros Organics and used to test the degradation performance of the samples. Furthermore, doubly distilled water was used throughout the experiment.

### 2.2. Synthesis method

The simple sol–gel method was used for the synthesis of the C-doped  $\text{TiO}_2$  and Sc and C co-doped  $\text{TiO}_2$ . In the typical synthesis method, 30 ml of ethanol, 5 ml water and 0.1 ml concentrated HCl were added to the flask adjusted with the mechanical stirrer. Furthermore, the TBOT was slowly added into the above solution under moderate stirring. After stirring for 2 h, 0.2 g of glucose was added as a carbon source into the mixture. The stirring was kept for another 4 h and then varied amounts of scandium nitrate were added as the scandium source and with the 5 h hours more stirring

to make sure that it was completely hydrolyzed and transformed into sol. In order to make the gel, the samples were aged for 10 h at room temperature. After the gelation completed, the samples were dried at 100 °C for 10 h and then calcined at 450 °C for 3 h.

The prepared samples were denoted as C- $\text{TiO}_2$  for carbon doped  $\text{TiO}_2$  whereas for Sc and C co-doped samples, they are denoted as x Sc/C- $\text{TiO}_2$ , where x is the amount of the scandium added in the sample in grams.

### 2.3. Characterization

X-ray diffraction (XRD) spectra for all the samples were collected in the range of 20–80° ( $2\theta$ ) by using Rigaku D/MAX 2550 diffractometer, operated at 100–200 mA and 40 kV. The approximate crystallite sizes of the prepared C-doped and Sc and C co-doped samples were calculated by using the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

Where  $D$  is the crystallite size of the samples to be calculated,  $K=0.89$  is a coefficient,  $\beta$  is the full width at half maximum (FWHM) of the diffraction [101] peak of anatase phase of  $\text{TiO}_2$ ,  $\theta$  is the diffraction angle, and  $\lambda$  is the wavelength of X-ray in nm corresponding to the  $\text{Cu K}\alpha$  ( $\text{Cu K}\alpha$  radiation,  $\lambda = 1.5406 \text{ \AA}$ ) irradiation. The UV–Visible absorption spectra were acquired as the dry-pressed disk of the samples using a Scan UV–Vis spectrophotometer (Varian, Cary 500) assembled with an integrating sphere assembly and applying  $\text{BaSO}_4$  as the reference sample for reflectance. The spectra were collected within the range of 200–800 nm at room temperature and standard atmospheric pressure. Perkin–Elmer PHI 5000C ESCA System instrument was applied for the XPS study of the prepared samples with Al  $\text{K}\alpha$  radiation source operated at 250 W. The shift of binding energy on the account of relative surface charging was standardized by using the C 1s level at 284.6 eV as an internal standard. The FTIR spectra were carried out by employing a Nicolet 740 FTIR spectrometer fitted with a TGS detector and a KBr beam splitter. Raman spectra of the prepared catalyst samples were recorded by using Renishaw inVia Raman spectrometer with the excitation wavelength of 514 nm at room temperature. The morphologies of samples were studied with the help of transmission electron microscopy (TEM, JEOL JEM2010). The specific surface areas and pore sizes of the samples were estimated with the assistance of BET equation (Micromeritics, ASAP 2020) by nitrogen adsorption at 77 K. Before the start of adsorption desorption measurements, the samples were degassed at 453 K for 10 h. The photoluminescence (PL) spectra were examined at room temperature with a Spectrofluorophotometer (Shimadzu, RF-5301) by applying Xe lamp as the excitation source at the excitation wavelength of 340 nm.

### 2.4. Measurement of photo-catalytic activity

The photo-catalytic activities of the prepared doped  $\text{TiO}_2$  samples were evaluated by calculating the degradation of 25 mg/L solution of AO7, which was recorded by the decolorizing of the solution in a particular time under irradiation. In a typical procedure, a homemade photo-reactor containing a wooden box was fitted with a quartz jacket condenser for the water circulation facility to refrain the system from heating up above 40 °C. A 500 W halogen lamp with the light density of 102 mW/cm<sup>2</sup> at the surface of the samples, was used as a light source. In order to stop the UV light and provide only visible light to the system, a glass optical filter was placed between the lamp and the degrading solution in the quartz tube to cut off the UV light with wavelength below 420 nm. The space adjusted between the lamp and center of the quartz tube

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