Synergistic effect between carbon dopant in titania lattice and surface carbonaceous species for enhancing the visible light photocatalysis

R. Kavitha, L. Gomathi Devi*

Department of Post Graduate Studies in Chemistry, Central College City Campus, Bangalore University, Dr. Ambedkar Street, Bangalore 560001, India

ABSTRACT

Visible light-sensitive carbon doped titanium dioxide ($C-TiO_2$) was prepared by grinding anatase TiO_2 with anhydrous D-glucose solution as carbon source followed by calcination. The catalysts were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), BET surface area measurements, scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS), FTIR analysis and photoluminescence (PL) techniques. The results confirmed the interstitial incorporation of carbon atoms in the TiO_2 lattice via O —Ti —C and Ti —O —C surface states. The calculation of valence band (VB) edge position of $C-TiO_2$ by using electronegativity values shows cathodic shift with increase in the carbon concentration and this renders high oxidative power for photogenerated holes. The observed new electronic state above the VB edge was responsible for the electronic origin of band gap narrowing and visible light photoactivity of $C-TiO_2$. The carbon atom was also present as carbonaceous species on the surface which acts as sensitizer. The photocatalytic activity of $C-TiO_2$ was evaluated for the degradation of 4-chlorophenol under both UV and solar irradiation. The undoped TiO_2 showed better activity under UV light whereas $C-TiO_2$ showed higher photocatalytic activity under visible light. The pretreatment of $C-TiO_2$ with UV light reduced the visible light activity due to the removal of surface carbonaceous species. The synergistic effect of surface carbonaceous species along with interstitial carbon is discussed in detail and accounted for visible light activity.

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Introduction

Titania has been regarded as the most promising photocatalyst due to its ability to completely mineralize the pollutants without other derivative chemicals. TiO_2 has attracted much attention due to unique optical and electronic properties which makes it suitable for the oxidation of organic pollutants [1]. The band gap excitation of titania under UV light promotes the transfer of electron from valence band (VB) to conduction band (CB). The photogenerated electrons and holes may take part in subsequent redox reactions with various ions/molecules adsorbed on the photocatalyst surface. The large band gap of TiO_2 (3.2 eV) and high degree of charge carrier recombination impair its practical applications under natural solar light [2,3]. The effective approach to tackle this challenge is to dope or co-dope TiO_2 with nonmetal elements such as C, N, S, I, B, P and F to extend the light absorbance of TiO_2 into visible region [4–6]. Among these dopants, carbon has received prominent importance. The visible light absorption in nonmetal doped titania is attributed to the incorporation of non-metal ion into TiO_2 lattice (i.e., doping) and also to the formation of chromophoric complexes at the surface (i.e., sensitization) formed by non-metal dopant source. Kisch et al. reported surface modification and interfacial sensitization mechanism by calcining TiO_2 in presence of urea [7]. Based on First Principle Calculations, it was shown that the carbon atom could replace either oxygen or titanium in the titania lattice depending on the concentration of oxygen present during the preparation process [8]. The carbon doping facilitates charge transfer process from bulk TiO_2 to the surface region via improving the extent of adsorption of organic pollutant molecules on the catalyst surface and increasing the conductivity of titania [9]. The formal oxidation state of carbon dopant ranges from −4 (carbides with Ti —C bond) to + 4 (carbonates with C —O bond) [8]. In the present work, we report the synthesis of carbon doped TiO_2 ($C-TiO_2$), and its photocatalytic activity was evaluated for the decomposition of 4-CP under UV/solar light irradiation.

Experimental

Materials

The $TiCl_4 \geq 99.9\%$ was obtained from Merck Chemicals, while anhydrous D-glucose ($C_6H_{12}O_6$) and 4-chlorophenol (4-CP) were supplied from SD Fine Chemicals, Bombay.

* Corresponding author.

E-mail address: gomatidevi_naik@yahoo.co.in (L.G. Devi).

Catalyst preparation

Anatase form of TiO_2 was synthesized by sol-gel route through the hydrolysis of $TiCl_4$ [10]. In a typical procedure, 25 mL of diluted $TiCl_4$ (100 mL of concentrated $TiCl_4$ was diluted to 1 L) with 1 mL concentrated H_2SO_4 was taken in a beaker and diluted to1 L. The solution pH was increased to 7–8 by the addition of liquor ammonia. The titanium hydroxide gel obtained is washed several times with double distilled water to make it free from chloride and ammonium ions. The gel was filtered, dried in an oven to remove adsorbed water molecules and then ground to a fine powder and it was calcined at 600 °C for 6 h. For the preparation of 0.04 wt% $C-TiO_2$, 0.00902 g of anhydrous D-glucose was dissolved in 25 mL double distilled water. Then, 2.5 mL of this solution is added to 1 g of TiO_2 and this mixture was ground in a pestle and mortar. The process of grinding is repeated for four times and the powder is finally calcined at 200 °C for 1 h to get $C-TiO_2$. Similar method was adopted for the preparation of $C-TiO_2$ with various dopant concentrations. The samples with 0.06, 0.08 and 0.1 wt% were abbreviated as $C-TiO_2$ (0.06 wt%), $C-TiO_2$ (0.08 wt%) and $C-TiO_2$ (0.1 wt%) respectively. With increase in the calcination temperature from 250 to 400 °C, the color of the samples turned white implicating the complete removal of carbon from TiO_2 lattice [11]. In order to confirm the role of surface carbon, the prepared $C-TiO_2$ sample was subjected to UV illumination for 1 h. The color of the $C-TiO_2$ changed from dark brown to light brown suggesting the elimination of only surface carbon under UV illumination and this catalyst is abbreviated as UV pretreated $C-TiO_2$ samples.

Catalyst characterization

The powder X-ray diffraction (PXRD) patterns were obtained using Bruker D8 Advanced diffractometer, which was operated at 30 kV and 20 mA using Cu Kα with nickel filter. The scan rate was varied from 2° to 0.5°/min to get X-ray diffraction line broadening. The Fourier transform infra red (FTIR) spectra were obtained using Bruker model Alpha–P IR spectrometer with diamond ATR cell. The X-ray photoelectron spectroscopy (XPS) measurements were carried out using AXIS ULTRA from AXIS 165, integrated with Kratos patented magnetic immersion lens along with charge neutralization system and spherical mirror analyzer. All binding energies were calibrated with respect to the carbon 1s peak at 284.8 eV. The diffuse reflectance spectra (DRS) were obtained using UV—vis spectrophotometer (Schimadzu-UV 3101 PC UV–vis-NIR) with $BaSO_4$ as the reference standard. The absorbance data were transformed into reflectance values and Kubelka–Munk method is used for the band gap measurement. The surface morphology was analyzed by scanning electron microscopy (SEM) analysis using JSM840 microscope operating at 25 kV on specimen upon which a thin layer of platinum had been evaporated. The nitrogen adsorption–desorption isotherms were recorded on a Nova Quanta Chrome Corporation 2006 Digisorb analyzer at liquid nitrogen temperature 77 K. The samples were degassed at 200 °C overnight prior to the measurement. The surface area was obtained by Brunner–Emmet–Teller (BET) method and pore size distribution was calculated from the adsorption branch of the isotherm by the Barret–Joyner–Halenda (BJH) model. The photoluminescence (PL) spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer. The reaction intermediates during the course of degradation reaction were analyzed from GC–MS technique using Thermo Trace GC Ultr, MS model Thermo DSQ II with electron impact ionisation and the chemical ionisation with mass range 1–1071 m/z.

Photochemical reactor

Experiments were carried out at room temperature using a circular glass reactor whose surface area is 176.6 cm^2, using 125 W medium pressure mercury vapor lamp as the UV light source. The photon flux

was found to be 7.8 mW/cm^2 by ferrioxalate actinometric method [12]. The emission wavelength falls in the region 350–400 nm, with maximum emission at 370 nm. No additional step was taken to eliminate the light of different wavelengths, since this process reduces the intensity of light. The irradiation was carried out by directly focusing light into the reaction mixture in the open air condition at a distance of 29 cm. All the experiments were performed using double distilled water. Solar light experiments were performed under sunlight directly between 11 a.m. and 2 p.m. when the solar intensity fluctuations were minimal and sunrays were not oblique. The experiments were conducted in the month of April–May at Bangalore, India. The latitude and longitude are 12.58 N and 77.38 E respectively. The average solar intensity was found to be 0.753 kW/m^2 (using solar radiometer). The intensity of the solar light was concentrated by using a convex lens and the reaction mixture was exposed to this concentrated sunlight. The solar radiation as a function of wavelength was measured by photometer, which shows a maximum at 450 nm. To compare the photocatalytic activity of all the catalysts, experiments were simultaneously conducted to avoid the error arising due to the fluctuations in solar intensity. A typical experiment contains 60 mg of photocatalyst dispersed in 250 mL of 10 ppm 4-CP solution. The reaction mixture was stirred vigorously using magnetic stirrer for entire time span of the experiment. Prior to irradiation, the reaction mixture was stirred for 30 min to ensure the establishment of adsorption/desorption equilibrium. The extent of adsorption is found from the equation; $Q = (C_0 - C)V/W$, where Q is the extent of adsorption, C_0 and C are the concentrations before and after adsorption, V is the volume of the reaction mixture and W is the amount of catalyst present in grams. The unit of Q is ppm mL mg^{-1}. Thirty minutes time period is selected as time to achieve a steady state adsorption level for 4-CP. The extent of adsorption did not change for prolonged time period. The 5 mL aliquots were collected from the suspension at definite time intervals and immediately centrifuged and filtered through 0.45 µm Millipore filter to remove the catalyst particles for spectrophotometric analysis. The residual concentration of 4-CP was determined by UV–vis spectrophotometer. A blank experiment containing only the pollutant 4-CP in the absence of photocatalyst under UV illumination was performed in order to determine the contribution of direct photolysis. The experimental results confirmed the absence of contribution from direct photolysis.

Results and discussion

PXRD studies

The TiO_2 was obtained by sol–gel technique in the present study. Anatase phase was found to be stable up to 600 °C, but further rise in temperature to 700 °C rutile phase formation takes place. During the calcination process around 450 °C the water content in the sample is completely eliminated and the crystallinity of the sample sets in and stabilizes in the temperature range of 450–550 °C and hence the sample was heated to 550–600 °C [10]. The diffraction peaks for TiO_2 and $C-TiO_2$ (with various carbon dopant concentrations) and the sample heat treated at 200 °C confirmed the anatase polymorph (Fig. 1). The average crystallite size was estimated based on broadening of (1 0 1) peak using the Scherrer's equation (1) and lattice strain (ϵ) was calculated from Eq. (2).

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

$$\varepsilon = \frac{\beta}{4\tan\theta} \tag{2}$$

where λ is the wavelength of Cu Kα source used, β is full width at half maximum (FWHM) of (1 0 1) diffraction plane, k is a shape factor (0.94) and θ is angle of diffraction. The X-ray diffraction peaks of crystal planes (2 0 0) and (2 0 4) of anatase were selected to determine