



Short communication

Low temperature synthesis of pure anatase carbon doped titanium dioxide: An efficient visible light active photocatalyst



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ABSTRACT

Low temperature pure anatase Carbon Doped Titanium Dioxide (C-TiO₂) is successfully synthesized by using starch as an effective, economical, and nonhazardous carbon source. The synthesized C-TiO₂ has been further characterized by X-Ray Diffraction, SEM, TEM, BET, XPS and UV-DRS techniques, which reveal that the particles are crystalline with spherical morphology, high surface area and an optical band gap of 2.79 eV for C-TiO₂ calcined at 400 °C. Furthermore photocatalytic degradation of Rhodamine B dye was carried out using as-prepared C-TiO₂ under visible light irradiation. Prepared C-TiO₂ calcined at 200 °C and 400 °C show higher degradation efficiency (85% and 100% in 120 min respectively) as compared to that of undoped TiO₂ and commercial Degussa P-25. Result shows that the C-TiO₂ containing lower carbon percentage has higher photocatalytic activity. Thus enhanced photocatalytic activity of C-TiO₂ may be due to synergic effect of carbon doping and [101] facet enhanced synthesis of anatase C-TiO₂.

1. Introduction

Recently photocatalytic oxidation by semiconductor nanomaterials has arisen as a promising technique to combat the growth of environmental issues with a significantly higher efficiency [1]. Along with this semiconductor nanomaterials have wide range of application in which Mole et al. successfully synthesized and explained structural as well as electrochemical properties of carbon doped Titanium oxide (C-TiO₂) electrodes with high conductivity and enhance double layer charging power [2]. Likewise Karthik et al. has fabricated the TiO₂ nanotubes by using the ethylene glycol, which was used for hydrogen production from water by photoelectrolysis [3].

TiO₂ is one of the most extensively employed semiconductors for the degradation and mineralization of many organic pollutants from the contaminated drinking water or industrial waste water sources but its wide optical band gap between valence band and conduction band restricts its photocatalytic activity to UV light only. To overcome this wide optical band gap of TiO₂, doping of TiO₂ with transition metals like Ag [4], Au [5], Mn [6], Fe [7,8], Co [9], Ni [10], Cu [11,12], Pd [13], has been extensively studied. However, except for a few cases, the photocatalytic activities of cation-doped TiO₂ decreases [14], because the transition-metal-doped TiO₂ suffers from an increase in recombi-

nation centers introduced by the dopant-related localized d-states in the band gap of TiO₂ [15] and poor photostability [16]. To overcome the problem of recombination of e⁻/h⁺ pair in TiO₂, non-metal dopants, such as nitrogen [17–22] and sulphur [23,24] are found to be more suitable as they generate the impurity state near the valence band edge, but do not act as charge carrier. This generated impurity state narrows the band gap and is responsible for inducing visible light photocatalytic activity in TiO₂ [16]. Further, the reports reveal that doping TiO₂ with carbon has an edge over non-metals in shifting the absorption band of TiO₂ in visible region [25–28]. Irie and co-workers prepared carbon-doped anatase TiO₂ powders by oxidative annealing of Ti-C under the flow of O₂ at 600 °C. The catalyst showed photocatalytic activities for the decomposition of 2-propanol to CO₂ via acetone under visible light irradiation (400–530 nm) [27], Sakthivel and Kisch synthesized C-TiO₂ by the hydrolysis of titanium tetrachloride with tetrabutylammonium hydroxide followed by calcination at 400 °C and 500 °C. In the degradation of 4-chlorophenol by artificial light (λ=455 nm) the catalyst powders have a high photocatalytic activities [25]. Recently, a C-TiO₂ with high surface area (204 m²/g) was prepared by temperature programmed carbonization of K-contained anatase TiO₂ under the flow of cyclohexane at temperatures between 450 °C and 500 °C [29].

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Despite abundant literature on the synthesis of C-TiO₂ nanostructures, all the C-TiO₂ was synthesized at high temperature. Therefore, there is need to develop a comparatively green and sustainable method for the synthesis of C-TiO₂ nanostructures comparatively at low temperature. Yun et al. reports the visible light photocatalytic decomposition of phenol using C-TiO₂ synthesized at low temperature (160 °C) and further calcinated at 350 °C [30].

Inspired by this low temperature synthesis, here we report, a fascinating method for the synthesis of C-TiO₂ nanostructures under mild aqueous condition. In proposed method we used starch as a carbon source as well as a capping agent. This low-temperature protocol for the synthesis of mesoporous C-TiO₂ involves use of starch and titanium tri-chloride (TiCl₃) as a carbon and Ti sources, respectively. We observe that, the reduction of starch to carbon is a results of the oxidation of Ti³⁺ to Ti⁴⁺, as no other reducing agent was used in this protocol during heat treatment. The resultant C-TiO₂ prepared by this novel approach exhibits much higher photocatalytic activity as compare to un-doped counterpart prepared by same method without using any carbon source.

2. Experimental

2.1. Materials

TiCl₃ (99.9%), Starch (99.9%) and Rhodamine B dye were purchased from Sigma-Aldrich, India. All chemical used in synthesis were of analytical grade and used without further purification.

2.2. Synthesis

Here we report the two-fold role of starch which acts as source of carbon as well as capping agent in reaction. Sol-Gel method was used for the synthesis of photocatalyst. 5 ml of 30% TiCl₃ was poured into beaker containing 500 ml of 1% starch solution with vigorous stirring. To this solution, excess ammonia (50 ml, 0.91 g/cm³) was added drop wise with constant stirring. After 20 min white colour precipitate of Titania was obtained, it was washed 3–4 times with de-ionised water and dried under vacuumed at room temperature. The resultant sample was named as C-TiO₂. This sample was divided into 3 parts; one part was kept as it is (C-TiO₂-RT), while other two were subjected to calcinations for 12 h at 200 °C (C-TiO₂-200) and at 400 °C (C-TiO₂-400), respectively.

2.3. Characterizations of photocatalysts

X-Ray diffraction (XRD) study of synthesized catalyst was carried out on X-Ray diffractometer (AXS D8 Advance Bruker, Germany) with Cu-K α radiation source ($\lambda=1.5406$ Å). Scanning Electron Microscope (SEM) along with EDAX were successfully verify by the JEOL Model JSM -6390LV. Transmission Electron Microscope (TEM) was determine by the PHILIPS Model CM200 with operation voltage 20-200kv. The High Resolution Transmission Electron Microscope (HR-TEM) was carried out on the FEI Model Tecnai G2, F30 with acceleration potential 300kv. XPS study were carried out on VG Microtech electron spectrometer using Mg Ka X-rays ($\lambda=1253.6$ eV) as the primary source of radiation. UV-visible diffuse reflectance spectra (UV-DRS) were recorded using a Jasco (model V-670) spectrophotometer. BET analysis was determined by using Micromeritics ASAP 2020 V3.04 H at -196 °C. UV-Visible Absorbance was recorded using Shimadzu UV 1800.

2.4. Evaluation of photocatalytic activity

Photocatalytic activity of all catalysts was evaluated by using the Rhodamine B dye as a model organic pollutant. Photocatalytic study was carried out using aqueous solution of Rhodamine B in homemade

photoreactor (30 cm H x 25 cm W x 25 cm L), which has centrally placed 250 ml round bottom flask and single 100 W tungsten filament lamp along with the magnetic stirring. The average intensity of 100 W tungsten filament light measured by digital lutron lux meter (model LX-101) was about 28000 lx. The photocatalytic activity of all samples was studied using 100 ml aqueous dye solution of Rhodamine B (50 ppm) and 25 mg photocatalyst under ambient conditions. This aqueous mixture was continuously stirred to get the uniform dispersion. Before irradiation of light, the dye solution and catalyst was stirred in dark for 30 min to allow adsorption-desorption equilibrium between catalyst and dye solution. Afterword the tungsten filament light was turn on for 120 min. During the course of reaction the 5 ml of reaction solution was removed for its analysis after the interval of 15 min and centrifuged immediately to remove the catalyst and further analysed by UV-Visible spectrophotometer at 554 nm, from which the photocatalytic degradation of Rhodamine B was studied. The same experiment was repeated for every sample.

3. Results and discussion

The structural characterization, crystallinity and phases form in prepared samples i.e. C-TiO₂-RT, C-TiO₂-200 and C-TiO₂-400 were performed by X-ray diffractometry (XRD). The X-ray diffractograms of prepared materials do not shows peaks for Rutile, brookite and any other impurities, which indicates the purity of obtained C-TiO₂ (Fig. 1). As shown in figure, the XRD of C-TiO₂-RT does not show sharp peaks, this is due to amorphous nature of TiO₂ and high carbon percentage on the surface of prepared samples as evident from EDAX data.

Since the graphitic carbon peak was not observed in XRD, the carbon seems to exist in elemental form on TiO₂ surface. After removing elemental carbon adhered on the surface of photocatalyst by combustion at 200 °C and 400 °C, the diffraction peaks of carbon could not determine by the XRD. However, the EDAX results [Fig. 2D, E, E] indicates that the prepared sample contains Ti, O and C elements thus detected carbon on C-TiO₂-400 is the carbon that had been incorporated into the TiO₂ framework and not on the nanoparticle surface. The interpretation of XRD shows the peak at angle (2 θ) of 25.45, 37.85, 48.12, 54.19, 55.04, 62.82, 68.97, 69.84, and 75.04 corresponding to the indices of (101) (004) (200) (105) (211) (204) (116) (220) and (215) planes respectively. The pattern could be assigned to a tetragonal anatase phase of TiO₂ [JCPDS No. 21-1272] with slight shifting of all peaks on higher side for C-TiO₂-400. The crystalline size of nanomaterials were successfully calculated from Debye-Scherrer equation [$D = 0.9\lambda / \beta \cos \theta$]. Whereas, λ is wavelength of used X-Ray radiations (0.15418 nm), β indicates the full width half maxima of peak and θ is for Bragg's angle of X-Ray diffraction peak. The average crystalline size of C-TiO₂-400 was found to be about 11 nm for

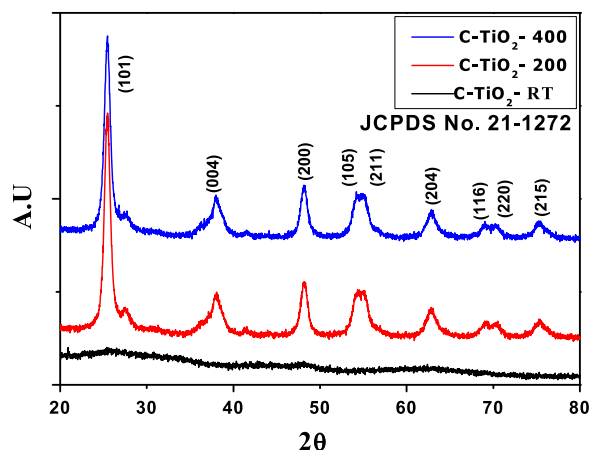


Fig. 1. X-ray diffraction patterns of prepared C-TiO₂-RT, C-TiO₂-200 and C-TiO₂-400.

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