



Copper and Nitrogen co-doped TiO₂ photocatalyst with enhanced optical absorption and catalytic activity



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ABSTRACT

Cu–N-codoped TiO₂ photocatalyst is synthesized by sol–gel method to obtain enhanced optical absorption in the visible region. Optimum concentrations of Cu and N were obtained by maximizing the photocatalytic activity for the monodoped (Cu or N) TiO₂. These optimized concentrations were used for synthesizing (Cu, N)–codoped TiO₂. The photocatalysts were characterized using XRD, micro-Raman, SEM, XPS, BET surface area analyzer, UV–vis diffuse reflectance spectroscopy and photoluminescence. XPS study suggests the incorporation of Cu²⁺ into TiO₂ lattice, which assists N to substitutionally replace oxygen in codoped TiO₂, while maintaining the anatase phase even after doping. N-doping creates minor variation in the energy band gap of TiO₂ reducing it upto 3.0 eV, while Cu doping was able to narrow the band gap to 2.2 eV mainly due to the localized levels of Cu-3d states and shifting of Ti-3d states to lower energy (due to oxygen vacancies) in the band-gap as deduced from XPS data and confirmed by the DFT calculation. In (Cu, N)–codoped TiO₂, visible light absorption is higher than the other TiO₂ samples, a feature that is mainly attributed to the formation of an isolated intermediate band (IB) occurring due to the strong hybridization between Cu 3d and N 2p orbitals. This IB contributes to visible light absorption by two step optical transition with the first transition from valence band (VB) to IB and the second from IB to conduction band (CB). The dopant species may also act to reduce the charge carrier recombination by acting as the trapping sites for photogenerated charges. (Cu, N)–codoped TiO₂ was able to degrade Methylene Blue dye and *p*-Nitrophenol solution under light irradiation with significantly better rate in comparison to monodoped and undoped TiO₂. High photocatalytic activity is attributed to the presence of IB in the energy band gap of TiO₂, which creates the synergic effect by higher visible light absorption and lower recombination of photogenerated charges.

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1. Introduction

Titanium dioxide (TiO₂) shows high photocatalytic activity among the semiconductor photocatalysts that have been investigated for the elimination of organic pollutants in aqueous or in the gas phase [1]. In addition, high chemical stability, environmental friendliness, easy availability, and cost effectiveness makes TiO₂ an ideal candidate as a photocatalyst [2]. Unfortunately, TiO₂ displays photoactivity only under UV light (wavelength <400 nm) due to its wide band gap (3.2 eV for anatase crystalline phase). Since the fraction of UV in the solar spectrum on the earth's surface is less than 5%, it is important to sensitize TiO₂ photocatalyst to absorb visible

light which would result in efficient utilization of the main part of the solar spectrum [3]. Therefore, increasing the efficiency of visible light absorption of TiO₂ is a subject of extensive current research. The previous research works provided some promising methods to enhance the photoactivity of TiO₂, involving metal or non-metal ions doping and co-doping [4].

Doping with metals like Cr, Fe, V, Mn, Cu, Zn, and Ni [5–8] reduces the energy band gap of TiO₂ and simultaneously reduces the recombination rate of photogenerated electron-hole pairs. However, at higher dopant concentrations these metals themselves become the cause of the recombination of photogenerated electrons and holes [9]. Doping TiO₂ with non-metallic anions such as N, S, and C, replaces O in the TiO₂ lattice to generate energy levels just above the top of the valence band of TiO₂ thus narrowing the band gap [10,11]. Even though, the band gap is reduced to a certain extent by low concentration monodoping (*p*-type or *n*-type), this narrowing is not enough for the efficient use of visible light. At higher

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concentration doping, it was experimentally observed that the impurity levels act as charge recerlinkAPCATB13817BIB0020[4].

Recently, the concept of second generation TiO₂ based materials was introduced where co-doping with two dopant elements produces a synergic effect to enhance the visible light absorption efficiency and reduce the recombination processes of the photogenerated charges [12–23]. Zhu et al. [12] have described a new idea of non-compensated *n*–*p* codoping which generates intermediate band (IB) in the mid gap of TiO₂ and increases both the thermodynamic stability and kinetics of charge carriers. Cr and N codoping was used as a model for non-compensated *n*–*p* codoping which showed increased visible light absorption and charge separation. Gai et al. [13] theoretically demonstrated that codoping of TiO₂ with passivated codopants such as Mo and C in charge-compensated condition shifts the Valance Band Maximum (VBM) up significantly, while leaving conduction band minimum (CBM) almost unchanged to satisfy the condition for hydrogen reduction in water splitting process. Several other combinations of dopants such as V–N, Cr–C, Fe–N, Zr–N, Si–Ni, etc. [14–18] have been studied in the past for various photocatalytic applications. Most researchers concentrated on codoping of metal and non-metal species where the former serves as *n*-type dopant while the later as *p*-type dopant. In this scenario, the dopants either produce charge compensation or provide net *n*- or *p*-type charge carriers. However, very few theoretical or experimental works are presented in literature where *p*-type metal is codoped with non-metal which also serves as *p*-type dopant. Metal species such as Cu²⁺, Ni²⁺, Co³⁺, and Fe³⁺ contribute charge carriers in the form of holes to convert TiO₂ from *n*-type semiconductor to *p*-type [19,20]. Song et al. [21] and Wang et al. [22] prepared (Cu, N)-codoped TiO₂ nanoparticles and investigated the influence of the amounts of Cu and N into co-doped TiO₂ on the photocatalytic activity. Co-doping of TiO₂ with N and Cu extends the absorption band up to 590 nm and produces higher photocatalytic activity than the pure N- or Cu-doped TiO₂ for the degradation of organic pollutants. In our recent article [23], the theoretical calculations carried out for *p*-type codoping of Cu and N in TiO₂ revealed the presence of an isolated in Intermediate Band (IB) deep in the band gap due to strong hybridization between Cu 3d and N 2p orbitals. The new IB is mostly responsible for high visible light absorption through a two-step optical transition. Nevertheless, experimental evidence is necessary in proving the ability of this codoped TiO₂ to be used as an efficient photocatalyst material.

The present work focuses on one of the second generation TiO₂ based materials, namely, (Cu, N)-codoped TiO₂, for its use in the photocatalytic degradation of organic pollutants from the aqueous media. The synthesis route used is sol–gel and the enhanced photocatalytic activity observed for (Cu, N)-codoped TiO₂ is discussed in terms of synergic effects produced by the presence of IB in its energy band gap.

2. Experimental methods

Sol–gel method was used to synthesize pure TiO₂ by using titanium (IV) butoxide (Ti (OCH₂CH₂CH₂CH₃)₄) and nitric acid (HNO₃) as precursor and catalyst respectively. Molar ratio of Ti (OC₄H₉)₄/H₂O/ethanol/HNO₃ was kept constant at 1/30/20/0.1. Ethanol (C₂H₅OH) and the precursor were mixed for 1 h at room temperature to form homogeneous mixture. Similarly, another solution mixture of de-ionized water, ethanol and HNO₃ was prepared under constant stirring. Later, water based solution was added drop wise into Ti precursor solution under constant stirring for 1 h. To enhance the homogeneity, the resulting solution was further stirred for 1 h at constant speed. To prepare N-doped TiO₂ triethylamine (N(CH₂CH₃)₃) was mixed with precursor, while for Cu-doped TiO₂ hydrated copper nitrate (II) was dissolved in

water based solution. Procedure used for Cu and N doping was combined to synthesized (Cu, N)-codoped TiO₂. For gelation, the resulting solution was left overnight at room temperature followed by drying at 100 °C for 3 h to remove excess solution. After grinding, the resulting powder was calcined in air at 500 °C for 2 h. Sample nomenclature used in the present work is shown in Table 1.

The surface morphology of all the samples was studied by scanning electron microscope (SEM–FEG, JSM 7001F, JEOL) equipped with energy-dispersive spectroscopy (EDS, INCA PentaFET-x3) to determine the composition of the samples. The structural characterization of the all samples was performed by X-ray diffraction (XRD) using Cu K α radiation ($\lambda = 1.5414 \text{ \AA}$). Raman spectra were recorded by using Renishaw micro-Raman spectrometer (RE-04) using solid state laser with the diode pumped at 514 nm. The band gap of the doped TiO₂ was determined by measuring the UV–vis absorption spectra (taken in diffuse reflectance mode), using Cary 500 UV–vis–NIR spectrophotometer, in the range of 200–800 nm. The surface composition and chemical states of the samples were examined by X-ray photoelectron spectroscopy using a SCIENTA ESCA200 instrument equipped with a monochromatic Al K α (1486.6 eV) X-ray source and a hemispherical analyzer. No electrical charge compensation was necessary to perform the analysis. Single point BET surface area of the powder photocatalysts was determined by nitrogen absorption at 77 K (Smart SORB 93) after degassing at 120 °C for 2 h. Photoluminescence (PL) study was carried out using fluorescence spectrophotometer (Varian; Cary Eclipse) where emission spectra were collected by exciting the photocatalyst with wavelength of 385 nm. To acquire PL spectra, 3 mg of powder photocatalyst was dispersed in aqueous medium of fixed amount and transferred into 1 cm \times 1 cm cuvette for measurement.

The photocatalytic activity of all the samples was evaluated by photodegradation of 0.01 mM methylene blue (MB) dye solution under light irradiation. 150 W Xenon lamp (Philips), which has spectrum nearly similar to solar spectrum, was used as the source of light. Photocatalytic degradation experiment was carried out using 50 ml of aqueous MB solution containing 20 mg of photocatalyst. The powder suspension was stirred for 30 min in dark to attain adsorption–desorption equilibrium of the molecules in the solution. The distance between the beaker and the light source was kept constant at 10 cm. After established time intervals, 1 ml MB aqueous solution was filtered out from the reactor vessel. The UV–vis adsorption spectra of the filtered solution were measured using the spectrophotometer. The photocatalytic activity was determined by measuring the normalized intensity of the absorption band of MB at 665 nm and plotting it as a function of time of irradiation (Fig. S1 of Supporting information). All the photocatalysis experiments were performed at room temperature and the pH of the solution was neutral during all the photocatalytic measurements. Similar type of experiment and measurement was performed for the degradation of transparent *p*-nitrophenol (*p*-NP) aqueous solution (10 ppm) where the absorption band at 320 nm was monitored with respect to time (Fig. S2 of Supporting information).

3. Results and discussion

In order to use the optimized concentration of Cu and N for codoping, TiO₂ was mono-doped with Cu or N using three different concentrations. As determined from the EDS analysis, the Cu atomic concentrations were approximately 0.5, 1, 2 at.% whereas, those of N were 1, 2, 3 at.% in TiO₂ for different samples. Low concentrations were used for doping because at high concentrations the same dopants behave as recombination sites for photogenerated charges thus decreasing the catalytic activity. The XRD patterns of TiO₂ mono-doped with Cu or N are presented in Fig. 1 along with the undoped TiO₂. The peaks observed at of 25.3°, 37.7°, 48.1°,

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