

RESEARCH PAPER

Mechanochemical Synthesis and Characterization of N-doped TiO₂ for Photocatalytic Degradation of Caffeine

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ABSTRACT

The present study reports the synthesis of N-doped TiO₂ photocatalyst for the degradation of caffeine using mechanochemical grinding method from the mixture of titania/urea followed by calcination at 400 °C. The phase composition, particle size, surface area, morphology and optical properties were characterized. The XRD results revealed that anatase is dominant and the size of crystal is decreased from 35.8 to 33 nm after mechanical doping. An improved surface area of 42.9 m²g⁻¹ is also reported. The morphology from SEM also showed a uniform yellow-like powder indicating complete dispersion of nitrogen on the TiO₂ surface. The prepared sample showed visible-light absorption in the region 430 nm corresponding to band gap energy 2.88 eV, indicating its potential applications as a visible light induced photocatalyst. Photocatalytic oxidation of caffeine were investigated in 300 minutes irradiation time and N-doped TiO₂ demonstrated the higher removal efficiency of 97% compared to commercial TiO₂ powder with 91% efficiency at the same experimental condition.

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INTRODUCTION

Mechanochemical synthesis is being widely applied to organic chemistry since quite long time, and mechanochemistry of inorganic solid is a well-established field in pharmacy, crystal engineering, material engineering, extractive metallurgy, agriculture and waste treatment [1]. Mechanochemical preparation procedure involves chemical activation of solid due to deformation and fracture which are technically induced by milling or grinding of the material [2]. The reaction proceeds with increase in the internal and surface energy, increase in surface area and decrease in coherence energy of the material involved which may lead to spontaneous aggregation, adsorption or recrystallization of the activated system during and after mechanical grinding [3].

Milling can be carried out in a variety of ways. The simplest ways are the laboratory motor and pestle and the laboratory vibrators which are efficient for small samples that do not require high energy barrier. Ball mills and high speed attritors are used for prolonged high energy milling [4].

The main advantage of mechanochemical synthesis is that it is a quantity process permitting kilograms of material to be produced at an ambient temperature, easy handling operation condition in solvent free mode and in very short processing time [5]. Mechanochemistry is also proved to be feasible alternative when dealing with highly insoluble reagents [6] and nanoparticles are often formed by this technological approach which adds value to process solids, simplification of the process, ecological safety with greener synthesis [7].

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Doping is one of the typical approaches to extend the spectral response of the wide bandgap semiconductors to visible light [8,9,10]. Successful doping can be achieved by many strategies with either transition metal ion or with non-metal dopants resulting in enhanced efficiency of the photocatalyst system [11]. Both of doped species can produce the impurity states lying between valence band and conduction band causing a narrow bandgap, but non-metal dopants minimizes the recombination compared to cation dopants [12]. Therefore, mechanochemical method can be employ to dope non-metal element into oxide fine particles.

Caffeine is found naturally in the leaves, seeds and/or fruits of at least 63 plant species worldwide. The most commonly known sources of caffeine are coffee, cocoa beans, kola nuts and tea leaves [13, 14]. Although it is found in many types of plants, the presence of caffeine in environmental water is largely attributed to discharges of domestic waste water [15]. Caffeine is largely expected to persist in the water, mainly due to its anthropic nature, distinctive origin, environmental destination, and elevated consumption [16].

In this paper, N-doped TiO₂ is synthesized by mechanochemical method and characterized for structural, morphological, optical and chemical nature. The photocatalyst is also tested for photocatalytic destruction of caffeine.

EXPERIMENTAL

Chemicals

Caffeine (99%, BDH), Titanium dioxide (98%) supplied from labtech India, and Urea CO(NH₂)₂ (BDH) were used for mechanochemical doping. Deionized water was used for the preparation of caffeine solution throughout the experiments.

Photocatalyst Synthesis

Commercial titania powder was mixed with 5% (wt) urea (CO(NH₂)₂) before being introduced into mechanical grinding using agate mortar and pestle followed by heating the milled sample at 400 °C in a muffle furnace for 1 hour. The grinding enabled the mechanochemical reaction between the components while the calcination allowed the enhancement of the binding strength as well as the removal of the unreacted starting material away from the surface of the oxide [17].

Photocatalyst Characterization

The crystalline structure of the photocatalyst was determined by X- ray diffraction using Philipps

X'pert X- ray diffractometer operated using CU-Kα radiation source at wavelength $\lambda = 1.5406\text{\AA}$. The data were collected for the range of 2θ between 20° to 120° . The morphology was recorded by scanning electron microscopy (SEM) recorded on JEOL JSM-5600. The Agilent Technologies (Cary630) FTIR Spectrophotometer was used in identifying the functional groups on the photocatalysts. The infrared spectra were measured from 400 to 1000 cm^{-1} at room temperature. The diffuse reflectance spectroscopy (DSR) of the photocatalysts was obtained using Perking Elmer Lambda 35 UV-Vis. Spectrophotometer and was used to characterize the optical properties of the samples. The spectra were recorded at room temperature from 200 to 800 nm and Kubelka–Munk relation was used to model the diffuse reflectance spectra into equivalent absorption spectra.

Photocatalytic Experiments

Photocatalytic experiment was carried out in an immersion well photoreactor shown in Fig. 1. A desired amount of photocatalyst was suspended into a caffeine solution in a photoreactor. The degradation reaction was conducted in the dark for 30 minutes in order to equilibrate the heterogeneous mixture. Subsequently, the solution was irradiated for 300 minutes and samples were taken at interval of 30 minutes for analysis using UV visible spectrophotometer. Each sample was passed through 0.45 μm Millipore membrane filter

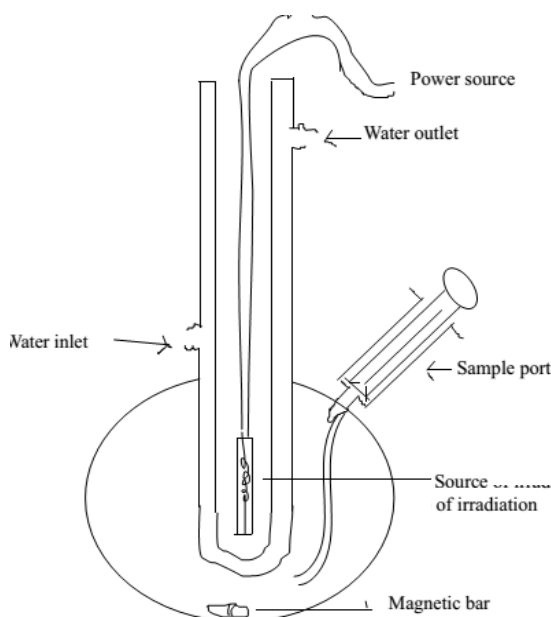


Fig.1: Schematic of an immersion well photoreactor

to remove the photocatalyst before the UV analysis. The percentage degradation was calculated using the formula below

$$\% \text{ Degradation} = \frac{C_0 - C_t}{C_0} * 100 \quad (1)$$

Where C₀ is the initial concentration of the caffeine and C_t is the concentration of caffeine at time (t).

RESULTS AND DISCUSSION

Photocatalyst Characterization

Figs. 2 and 3 show the XRD pattern of the pure titania powder and the N-doped TiO₂ prepared by mechanochemical doping respectively. Based on the spectra, the strong diffraction peaks representing the anatase phase (JCPDS 21-1272) are observed at 2θ values of 25.6°, 38°, 48.32°, 54.14°, 55.83°, 62.92° and 75.28 ° for N-doped TiO₂ as well as peaks at 25.78°, 38.24°, 48.48°, 54.3°, 64.1°, and 75.48° for

pure TiO₂. This confirmed that the anatase phase is dominant and this is beneficial since anatase TiO₂ is reported to be more photocatalytically active than rutile [18,19, 20]. The prepared N-TiO₂ peak broadened after mechanical doping and the size of the crystals also decreased compared to the pure TiO₂. This can be attributed to formation of nanoparticles and aggregation of the crystallites as they get smaller that is in agreement with other reported studies [21, 22]. The sharpness of the peaks in the spectra can also be attributed to the calcination process which is believed to induce high crystallinity [18]. The absence of spurious diffractions indicates the crystallographic purity and the lack of peak of the doping specie also indicates its complete dispersion on the surface of the oxides [23]. The average particle size has been estimated using Debye-Scherrer formula (equation 2). The surface state was also established from equations 3 and 4 as presented in Table 1.

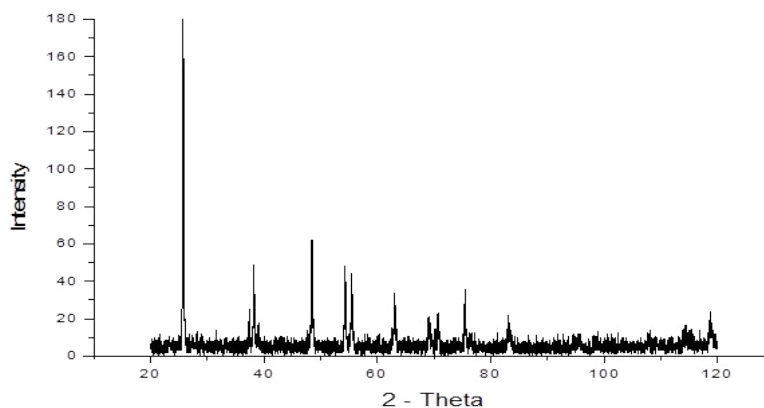


Fig.2: XRD Pattern for TiO₂

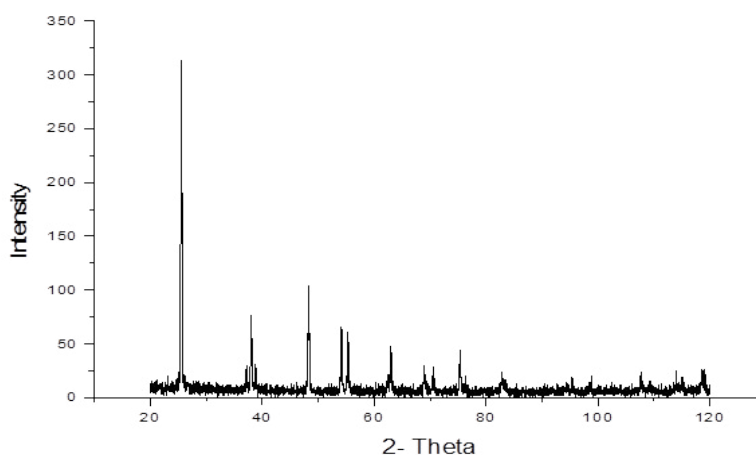


Fig.3: XRD pattern for N-TiO₂

Table 1: Some properties of the photocatalysts

Photocatalysts	Average size(nm)	SA m ² g ⁻¹
TiO ₂	35.8	39.6
N-TiO ₂	33	42.9

$$SSA = \frac{SA}{V \times \rho} \quad (3)$$

$$SSA = \frac{6000}{D \times \rho} \quad (4)$$

It is observed that the prepared N-doped TiO₂ has smaller particle size and larger surface area compared to pure titania powder and should facilitate the faster photoreaction between TiO₂ and the interacting media which mainly occurs at the interface and strongly depends on the surface area of the material [24].

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (2)$$

Where λ is the wavelength of X-Ray (0.1540 nm), β is FWHM (full width at half maximum), θ is the diffraction angle, SSA is the specific surface area, V is the particle volume and SA is the surface area, D is the size (average size), and ρ is the density of TiO₂ (4.23 g.cm⁻³).

The surface morphology by SEM of TiO₂ and N-doped TiO₂ is presented in Figs. 4 and 5, respectively. The growth of the mixture of yellow

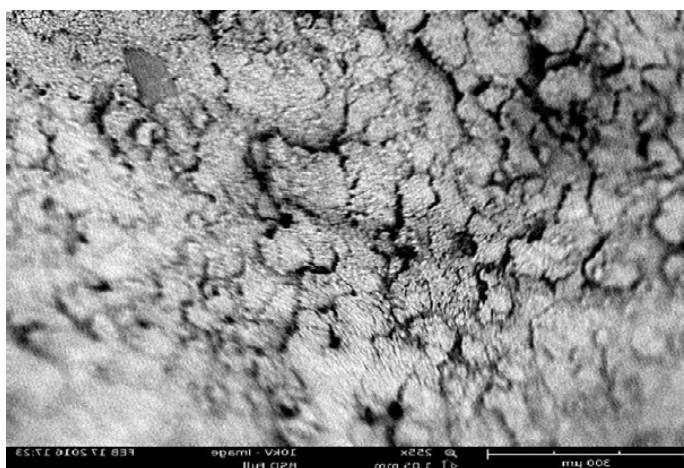


Fig. 4: SEM image of TiO₂



Fig. 5: SEM image of N-TiO₂

like mass of N-doped TiO₂ can be clearly seen from the SEM image of the doped photocatalyst. The uniformity of the observed yellow like powders in the morphology of prepared N-TiO₂ indicates complete dispersion of nitrogen on the TiO₂ surface. The difference in morphology observed in the N-doped TiO₂ particles is indicative of the decomposition of the nitrogen precursor in accordance with the previous study [25]. Thus, the remaining unwanted material was necessarily decomposed during calcination and N-doped TiO₂ would be finally obtained.

The FT-IR analysis was used to characterize the functional groups of the photocatalysts. The spectra are shown in Figs. 6 and 7 for pure TiO₂ and N-doped TiO₂, respectively. Generally, the prepared

photocatalyst had similar curves indicating the effectiveness of the mechanochemical doping with nitrogen which did not result in the formation of other compounds as reported in the literature [26]. Fig. 7 confirms the substitution of crystal lattice O to N species occurred by nitration using urea molecule that resulted in the formation of N-Ti-O bond. The strong absorption band in the region 400 to 600 cm⁻¹ in the spectra of pure TiO₂ and N-doped TiO₂ has been assigned to the -Ti-O- stretching [17]. The intensity of the absorption bands of the prepared N-doped TiO₂ are stronger, broader, and are in close proximity compared to that of pure titania. This indicates that N-doped TiO₂ sample contains more water and hydroxyl groups

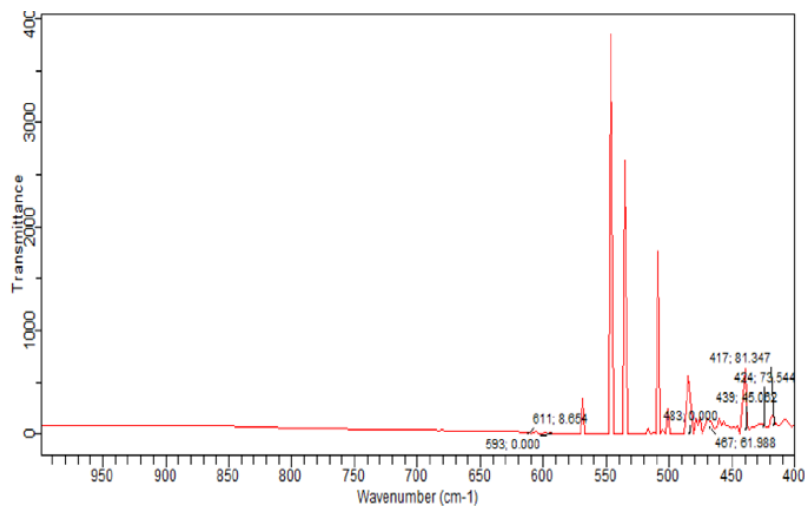


Fig.6: FTIR spectra of TiO₂

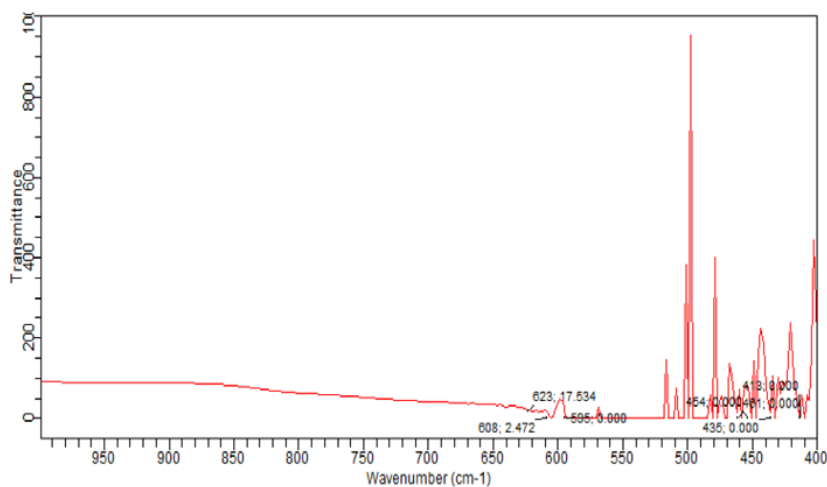


Fig.7: FTIR spectra of N-TiO₂

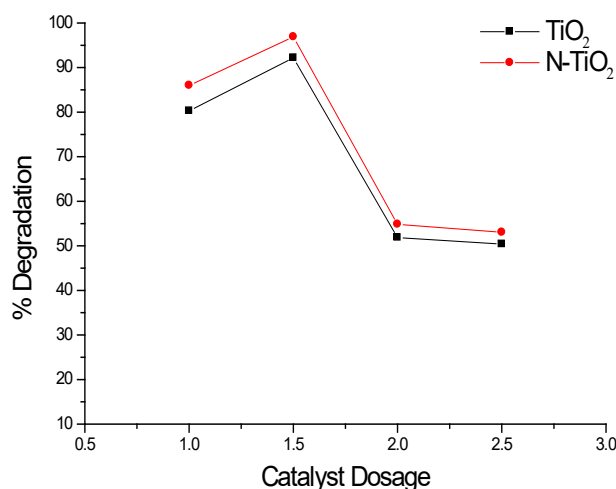


Fig. 8: Influence of the photocatalysts on the degradation of caffeine. Initial caffeine conc.: 30 mg/l, pH: 6.9, irradiation time: 300 minutes.

which play an important role in photocatalysis through interactions with photogenerated holes giving better charge transfer and inhibiting the recombination of electron-hole pairs [27]

The UV-Vis spectrum revealed that N-TiO₂ depicts higher wavelength for the absorption band at 430 nm corresponding to band gap energy 2.88 eV compared to pure TiO₂ showing highest absorption at wavelength of 383 nm which is relevant to the band gap structure of anatase TiO₂ (3.23 eV). This shift in the absorption band in N-TiO₂ is attributed to color change from white to yellowish due to mechanochemical doping of nitrogen. Therefore, this clearly indicates the significant of nitrogen doping on the band structure of TiO₂.

Photocatalytic Degradation of Caffeine

To explore the effect of mechanochemical doping of material during the photocatalytic degradation of caffeine, the prepared N-TiO₂ was compared with pure TiO₂ with equivalent concentration of the both photocatalysts for the degradation efficiency at the same experimental condition. Fig. 8 shows 97% caffeine degradation over a doped system, whereas the degradation over TiO₂ produces a degradation of 91% even at 300 minutes irradiation time and optimum photocatalyst dosage of 1.5 g/l. This can be explained in terms of the interaction between TiO₂ and doping material, as well as the difference in morphology and structure from TiO₂ bulk. Considering the surface analysis result, the N-doped TiO₂ photocatalyst sample having a larger surface area could allow a larger amount of

surface adsorbed species in which photocatalytic degradation strongly depends on.

CONCLUSIONS

A visible light responsive N-doped TiO₂ photocatalyst was obtained by mechanochemical grinding method using mixture of urea/titania followed by calcination at 400 °C. Photocatalytic efficiency of pure TiO₂ and prepared N-doped TiO₂ photocatalysts exhibiting within 300 minutes of standard visible light irradiation was tested for the degradation of caffeine, and degradation efficiencies of 91 and 97% were obtained, respectively. Therefore, mechanochemical activation is proved to be an effective procedure where an improvement in technological process can be attained via combination of several effects which influence the properties of applied solid and can be used as an alternative to more conventional often solution-based preparative strategies.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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