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Effective catalytic performance of manganese and phosphorus co-doped titania nanocatalyst for Orange-II dye degradation under visible light irradiation

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ABSTRACT

Co-doped nano titania was prepared by doping with varying weight percentages of phosphorus (P) and manganese (Mn) by sol–gel method for eventual application in degradation of dyes. Co-doping reduces the band gap of TiO_2 and shows an effective degradation of dye in visible light. The as prepared catalysts were characterized by X-ray diffraction spectroscopy (XRD), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectroscopy (UV–DRS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and fourier transform infra red spectroscopy (FT-IR). The XRD data of the catalysts revealed that the synthesized samples were in anatase phase with 2θ at 25.3°. The XPS results indicated that the P and Mn were present in TiO_2 as P^{5+} and Mn^{4+}/Mn^{3+}. UV–DRS spectra showed a significant absorption shift from ultraviolet to visible region. The doping pattern of P and Mn in TiO_2 were determined by FT-IR, the stretching frequencies attributed that they have substituted Ti in TiO_2 lattice. Based on TEM results the particle sizes were found to be ranging from 6.8 to 9.6 nm. Photocatalytic efficiency of synthesized nano materials was tested with non-biodegradable Orange-II, an azodye pollutant under visible light. The kinetics of degradation of the dye was studied under different conditions such as pH, catalyst dosage, dopant concentration, initial dye concentrations and finally optimum conditions were established. The P/Mn co-doped TiO_2 showed better (11 fold) photocatalytic performances than undoped TiO_2. The reactive species such as OH radicals which are formed in the reaction were tested by photoluminescent spectroscopy (PL).

Introduction

TiO_2 in anatase form was proven to be more suitable for environmental applications due to its high photo reactivity [1,2]. But it exhibits intrinsic drawback of high band gap making it active only in less available ultraviolet region. This severely limits its widespread applications. Shifting of optical absorption of TiO_2 from ultraviolet to visible spectral range will have a profoundly positive effect in harnessing solar radiations. To make it possible, many efforts have been made to narrow the band gap by doping TiO_2 with various non-metals [3–10] and metals [11–15]. Recently co-doping has attracted much interest since co-doped TiO_2 exhibited better performance in its applications when compared with single doped titania [16–18]. According to literature survey, the functionality of non-metal dopant is to shift the absorbance region of TiO_2 from ultraviolet to visible light region, besides narrowing the band gap of TiO_2 and the functionality of metal dopant is to facilitate the charge separation of free electrons, energized holes and to decrease their rate of recombination [19,20]. Besides, considering the significance of visible light responsive photocatalyst, it is very interesting to search for new photocatalyst with appropriate crystal phase, particle size and other surface properties to improve the photocatalytic activity. Among non-metals, phosphorus (P) doping is typical and found to be the most effective dopant for photocatalytic applications [21,22]. Many investigations have been carried out on P doped TiO_2 and studied its effect on surface area, thermal stability and oxygen vacancies, thus improving the photocatalytic performance [23–25]. Earlier studies on manganese (Mn) doped TiO_2 focussed primarily on its magnetic properties and electronic states [26–28]. Very few investigations studied on role of manganese in photo-catalytic degradation of organic pollutants [29,30]. Hence, we have

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selected phosphorus and manganese as co-dopants to understand its cumulative effect on photocatalytic activity of TiO_2.

Various methods available for the preparation of TiO_2 photocatalyst include precipitation [31], hydrothermal, solvothermal [32], chemical vapour deposition [33], electrospinning [34] and so on. Among all the methods available, sol–gel method is advantageous because powders of homogenous concentrations and high purity can be synthesized at very low temperatures under stoichiometry control [35]. Hence, in our research sol–gel method was chosen for the synthesis of P/Mn co-doped photocatalysts. A model pollutant Orange-II dye was selected in order to check the photocatalytic activity of as prepared photocatalysts in visible light. Orange-II is non-volatile compound, soluble in water and does not undergo bio-degradation in waste water treatment plants [36]. In the literature it was degraded by several processes [37] and with various catalysts like ZnO, Eu/TiO_2 [38,39].

Experimental

Synthesis of photocatalysts

A series of TiO_2 samples were prepared by co-doping with phosphorus and manganese in the range of 0.25–1.00 wt.% along with undoped TiO_2 by sol–gel method [40]. For preparation of undoped TiO_2 ethanol is taken as solvent and water was added to titanium tetra-butoxide (titanium precursor) for hydrolysis and condensation reactions were taken place in presence of nitric acid. In case of co-doped catalyst preparation, calculated quantities of manganese nitrate and triethylphosphate, precursors of P and Mn were first dissolved in ethanol along with water and the resultant solution was added drop by drop to the ethanol solution of $Ti(OBu)_4$ under vigorous stirring. After complete addition, the colloidal suspension was allowed to stir for 90 min and aged for 48 h. Thus obtained gel was dried in an oven at 70 °C. Later, it was well grinded and calcined at 400 °C for about 5 h in muffle furnace at the rate of 2°/min. Then, cooled in a desiccator and ground to form homogenous powder. Finally depending on the dopant concentrations light grey to dark grey coloured powders were obtained.

Characterization of photocatalysts

To identify the crystal phase of synthesized samples XRD spectra were recorded for 2θ from 20 to 80° with model Ultima IV, RIGAKU diffractometer using monochromatized CuKα radiation (λ = 1.541 A°) with a germanium solid state detector. An accelerating voltage of 35 kV and emission current of 30 mA were used with a step time of 2° min^{-1}. The valance state of doped elements in the photocatalysts were determined by XPS studies using PHI quantum ESCA microprobe system model, using AlKα radiation of 250 W X-ray tube as a radiation source with energy of 1486.6 eV, 16 mA × 12.5 kV under working pressure lower than 1×10^{-8} N/m^2. All the spectra are corrected by taking carbon peak at standard value of 286.4 eV. The fitting of the XPS curves were analysed with multipack 6.0A software. UV–vis absorption spectra of the samples were obtained by using Shimadzu 3600, UV–vis NIR spectrophotometer equipped with an integrating sphere diffuse reflectance accessory, using $BaSO_4$ as reference scatter. Powder samples were loaded in a quartz cell and spectra was recorded in the range of 250–800 nm. Surface morphology studies were carried out using scanning electron microscope (JSM-6610LV) operated at 20 kV. The size and shape of the nanoparticles were recorded with a TECNAI FE12 TEM (Eindhonen, The Netherlands) instrument operating at 120 kV. In each image, more than 100 particles were analysed with Cool Ruler software to measure the particle size. FT-IR spectra were taken by Thermo Nicolet Nexus 670 spectrophotometer by using KBr as reference sample. Photoluminescent spectral analysis was done using Horiba Jobin Fluoro Max-4 instrument with a PMT voltage of 150 V and slit set both at 2.5 nm.

Photocatalytic activity of catalyst

The photocatalytic efficiency of the synthesized co-doped and undoped TiO_2 was checked by degrading a model azo-dye pollutant, Orange-II using visible light in a photoreactor system. High pressure mercury vapour lamp (Osram, India) of 400 W was used as visible light source of 35,000 Lumen (output is 436–546 nm) with UV filter positioned parallel to the reaction vessel. The distance between the light and the reaction mixture was 20 cm. Cut off filter 51,472 was placed in the path of light for complete removal of UV radiation and running water was circulated around the sample container to filter IR radiation. However, detailed description of photoreactor is given elsewhere [41]. Dye solution with catalyst was stirred in dark for 20 min to establish adsorption/desorption equilibrium condition on the catalyst surface and exposed to visible light. At certain regular time intervals, 5 mL aliquots of samples were collected through 0.45 μm Millipore syringe filter. The filtrate was analysed on spectrophotometer at a wavelength of 484 nm. To have a comprehensive comparison, the reaction environment is maintained same for all the activity tests. The percentage of degradation of dye was calculated from the following equation:

$$\% \text{ of Degradation} = \frac{A_o - A_t}{A_o} \times 100$$

where A_o is initial absorbance of dye solution before degradation and A_t is absorbance of dye solution at time t.

Results and discussion

XRD studies

The functionality of TiO_2 for different applications depends on its crystal phase. For photocatalytic applications anatase phase is preferred. The XRD patterns from 2θ = 20–80° of P/Mn co-doped TiO_2 nanopowders calcined at 400 °C is shown in Fig. 1. The X-ray diffraction peak at 25.3° corresponds to the characteristic peak of crystal phase (1 0 1) of anatase for all the synthesized samples. The XRD patterns of all the samples exhibit typical peaks at 2θ = 25.3°,

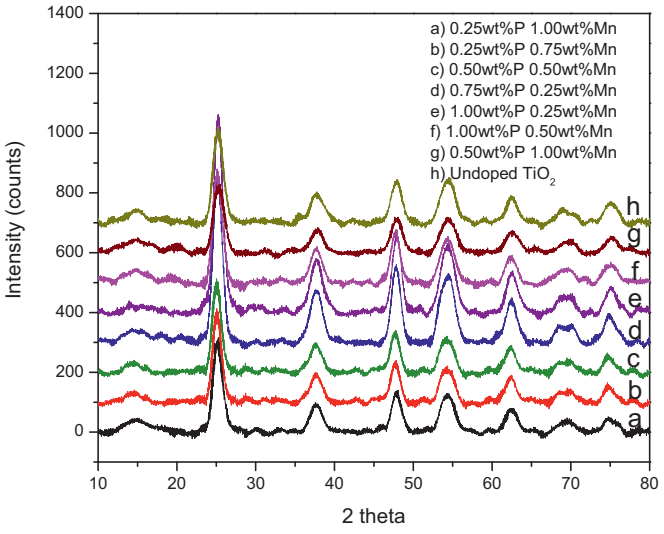

Fig. 1. XRD patterns of phosphorus and manganese co-doped TiO_2 photocatalyst.