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Surface modified Nd doped TiO_2 nanoparticles as photocatalysts in UV and solar light irradiation

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Abstract

Nd doped TiO_2 nanoparticles were synthesized by sol–gel method exhibiting photocatalytic activity in solar light together with UV light irradiation. Photoactivities of the catalysts were investigated in terms of degradation of Methyl Orange dye. 1.0% Nd doping appears to be optimum, yielding highest degree of degradation. Ag coating on 1.0% Nd doped sample is seen to further improve the performance of the catalyst. Nd doping and Ag coating could be ensured through the EDAX analysis of the sample. The morphological investigations of the samples reveal the presence of nanoparticles with average size of ~8 nm. The improvement in the optical properties of TiO_2 on Nd doping and Ag coating was confirmed by Diffuse Reflectance UV–Visible (DRUV) and Photoluminescence (PL) spectroscopy. The decrease in the PL intensities together with increase in visible absorption peaks in DRUV spectra of the Nd doped and Ag coated sample implies improvement in the optical properties in comparison with undoped TiO_2. Doped and coated samples exhibited high surface area than the undoped sample which was ensured by the BET surface area analysis.

Keywords: TiO_2 nanoparticles; Nd doped; Ag coated; Methyl orange; Solar light activity; HPLC analysis

1. Introduction

Efficient utilization of solar energy is a foremost objective of the scientists and engineers of 21st century. In addition to that, environmental pollution due to the release of toxic chemicals from industrial sectors is of major concern in recent years. Photocatalysts can effectively convert solar energy into chemical energy which can be used for decomposing toxic organic and inorganic pollutants to purify water and air (Sharma et al., 2012). The most often used photocatalyst due to its optical and electronic properties, stability, low cost and non toxicity is TiO_2 (Burda et al., 2003; Diwald et al., 2004; Li et al., 2005; Shankar et al., 2008). However, its large band gap (3.2 eV) and high rate of electron–hole recombination limits its efficiency only up to UV light region (Wahi et al., 2005). Since the fraction of UV in the solar spectrum is less than 5%, TiO_2 cannot efficiently exploit the abundant natural resource, i.e. solar radiations, which dominantly consist of visible light. Hence, development of solar light active photocatalytic materials is a subject of extensive current research in this field.

Doping TiO_2 with transition metals having '*d*' electronic configuration (Kato and Kudo, 2002; Yu et al., 2002) or non-metals such as Nitrogen (Gole et al., 2004), Boron (Begum et al., 2008) and Sulphur (Rockafellow et al., 2009) is known to enhance their response in the visible light region. Few reports are also available accounting for the improvement in the efficiency of TiO_2 towards visible light when doped with lanthanide ions/oxides with $4f^n$ electron configuration (Parida and Sahu, 2009). Amongst the few

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lanthanides (Pr^{3+}, Nd^{3+}, and Dy^{3+}), that exhibit absorption in the visible light region, Nd^{3+} has maximum absorption due to 4*f* electron transition (Jiang et al., 2010). Hence, Nd doping has been attempted in TiO_2 nanoparticles which improve the efficiency of catalyst by reducing the band gap of TiO_2 and thereby facilitating strong electronic transitions in the visible region.

Further, noble metals such as Ru (Houskova et al., 2009), Pt (Kim et al., 2005), Au and Ag (Rupa et al., 2009) when deposited or doped on TiO_2 contribute towards electron–hole separation and promotes the interfacial electron transfer process as they possess high Schottky barriers, thus act as electron traps (Loganathan et al., 2011). As per the work functions, the height of Fermi energy level is Ag > Ru > Au > Pt (Shen et al., 2010). Therefore, loading a small amount of silver on highly active Neodymium (Nd) doped TiO_2 was thought to increase the effectiveness of catalyst in terms of its photocatalytic activity.

The present paper reports the synthesis and photocatalytic activity of Nd doped and silver coated TiO_2 photocatalysts prepared by sol–gel and photodeposition methods respectively. These catalysts were characterized by XRD, FTIR, Surface area, DRUV, Photoluminescence, SEM and TEM. The photocatalytic properties of all the samples were tested by monitoring the degradation reaction of Methyl Orange (MO) in sunlight as well as in the UV light.

2. Experimental section

2.1. Catalyst preparation

All the chemicals used were of analytical grade. Titanium isopropoxide was supplied by Avra synthesis Pvt. Ltd. India. The salt precursor, i.e. Neodymium oxide (Nd_2O_3), was from Alfa Aesar (Johnson Matthey Chemicals) India. Double distilled water was used for synthesis. TiO_2 was prepared by starting with stoichiometric amount of Titanium isopropoxide dissolved in appropriate amount of ethanol under vigorous stirring. To this, 2–3 drops of nitric acid were added to obtain a clear solution; the solution was then hydrolyzed with distilled water for 45 min to obtain the sol of TiO_2. The sol thus formed was subjected to aging for a period of 24 h under ambient conditions. The resulting gel was then heated at 100 °C by keeping it in an oven for 48 h. This dried powder was further sintered at 500 °C for 3 h to get the desired phase of TiO_2.

Nd doped (0–5.0%) TiO_2 samples were prepared by the following process: Two sets of solutions were prepared initially. Solution-A consisted of stoichiometric amount of Titanium isopropoxide dissolved in appropriate amount of ethanol along with 2–3 drops of nitric acid and Solution-B consisted of stoichiometric amount of neodymium nitrate (Neodymium oxide was dissolved in nitric acid) dissolved in a mixture of ethanol and water (10:1). Solution-B was added dropwise to solution A under vigorous stirring at room temperature. After complete addition, the mixture was stirred for additional few minutes. The remaining procedure was similar as mentioned above.

Silver Deposition: Silver was deposited on 1.0% Nd doped TiO_2 by photodeposition method. For this, 50 mg of sample was taken in a mixture of distilled water and ethanol (5:1). To this, 1 ml of 0.005 M $AgNO_3$ solution was added. This mixture was then photoirradiated under 80 Watt high pressure Hg lamp for 2 h. The doping was confirmed in terms of change in colour of sample from faint blue to grey black. The reaction mixture was then filtered and the products were dried by keeping them in an oven for 3 h at 100 °C. Ag coated 1.0% Nd doped sample will be referred as coated sample in the further text.

2.2. Characterization

The *FTIR* analysis of the samples were carried out in the region ~4000–400 cm^{-1} on *FTIR* Shimadzu 8400 instrument. KBr was used as mulling agent for preparing the samples. The X-ray diffractograms were recorded on a Bruker AXSD-8 advance X-ray diffractometer with monochromatic Cu Kα radiation ($\lambda = 1.5406$ Å). Silicon was used as an external standard for correction due to instrumental broadening. The diffuse reflectance UV–visible absorption spectra of the samples were recorded on a UV–visible spectrophotometer (Perkin–Elmer LAMBDA 950). The photoluminescence (PL) spectra of the solid samples were recorded at room temperature by using PL – Perkin–Elmer LS-55 spectroflurometer. The spectra were recorded in the range of 375–500 nm with an excitation wavelength of 345 nm. Surface areas of the samples were measured on Smart Sorb 91 “BET” Surface Area Analyzer. N_2 was used as the adsorbing gas. EDAX and Scanning Electron Micrographs (SEM) of the samples were taken on an analytical instrument (JEOL-JSM 6360 A). SEM’s were recorded by coating the pellets and films of the samples with Ag–Pd alloy using vapour deposition method. Transmission electron microscopic (TEM) images of the samples were observed under the Philips CM-200 instrument at an accelerating voltage of 200 kV. The suspension of the sample in ethanol was loaded on carbon coated copper grids of 200 mesh size. The grids were dried under the IR lamp and viewed under the microscope.

2.3. Photocatalytic activity

The photocatalytic activities of all the catalysts were tested by studying the degradation reaction of Methyl Orange. A high pressure mercury lamp (80 W) was used as a light source placed in the photoreactor surrounded with water circulated quartz jacket to avoid thermal heating. Aqueous solution of dye (7×10^{-5} M) with 50 mg of catalysts was used for photolysis experiments. Air saturated suspensions (dye + catalysts) were exposed to UV and solar light radiations for studying the photodegradation reaction. Prior to photoreaction the suspensions were magnetically stirred in a dark condition for 30 min to