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Synergistic effect of Ag deposition and nitrogen doping in TiO_2 for the degradation of phenol under solar irradiation in presence of electron acceptor

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ABSTRACT

Ag deposited nitrogen doped TiO_2 (Ag–$TiO_{2-x}N_x$) was prepared using sol gel titania by grinding it with stoichiometric amount of Urea as nitrogen source followed by the photoreduction of Ag^+ to Ag^0. These samples were characterized by powder X-ray diffraction (PXRD), UV-visible absorption spectroscopy, Fourier transformed infrared spectroscopy (FTIR), photoluminescence (PL) and scanning electron microscope (SEM). PL analysis of the samples indicated that the electron-hole recombination has been effectively inhibited after the Ag deposition on TiO_2 and $TiO_{2-x}N_x$. Ag–$TiO_{2-x}N_x$ exhibits much higher visible-light photocatalytic activity when compared with N-doped or pristine TiO_2. The catalysts along with the oxidants can accelerate electron transfer process and inhibit the fast electron-hole recombination. The observed high process efficiency (Φ_λ) of Ag–$TiO_{2-x}N_x$ particles compared to $TiO_{2-x}N_x$ and pure TiO_2 photocatalyst can be accounted to the synergistic effect of Ag loading along with N doping. Strongly interacting electron accepting species such as hydrogen peroxide and ammonium persulphate chemisorbed at the photocatalyst surface are said to act like surface states enabling inelastic transfer of electrons from the conduction band to the oxidizing species. The electronic states of different energies within the band gap have a major role in enhancing the efficiency.

1. Introduction

Titanium dioxide (TiO_2), is a chemically stable, nontoxic, highly efficient, and relatively inexpensive photocatalyst, which is widely used for water and air purification [1–3]. Under the UV irradiation an electron (e^-) gets excited to the conduction band (CB), leaving a hole (h^+) in the valence band (VB). These electrons and holes can initiate redox reactions on the surface of TiO_2. The practical applications of TiO_2 have been suppressed by the low quantum yield that arises from the rapid recombination of photo-induced charge carriers and the other drawback is the poor solar absorption efficiency that is determined by its band gap. It was found that doping with nonmetals (e.g., boron [4], carbon [5], nitrogen [6] and fluorine [7]), especially nitrogen can successfully modify the electronic structure of TiO_2, extending the photoresponse of TiO_2 to the visible light region. Many studies have been reported that loading of noble metals (e.g., Pt, Au, or Ag) on the surface of TiO_2 can effectively hinder the recombination and promote the transfer of photo-induced electrons to these metal deposits [8–12]. Tian et al. reported that nitrogen doping followed by Au metallization leads to the synergistic effect to enhance the visible-light photocatalytic activity of TiO_2 for the degradation of methylene blue and 2,4-dichlorophenol [13]. The photoresponse of TiO_2 is extended to the visible light region by the nitrogen dopant and the loaded noble metal hinders the recombination of electrons and holes. Silver occupies exceptionally special position among the various metals from the point of view of its electronic properties. The work function of the silver (ϕ = 4.3–4.7 eV) is much lower than the work function of the other noble metals especially gold Au (ϕ = 4.8 eV) and Pt (ϕ = 5.3 eV). These metals are capable of forming Schottky barrier at the surface of TiO_2. Fermi levels of Au and Pt are located far below the position of conduction band edge of TiO_2. Electrons can only flow in one direction from TiO_2 to the metal deposit and facilitate the charge separation. In case of silver, Fermi levels are much closer to the conduction band edge of TiO_2 and the electrons can flow in both the directions. Other exceptional properties of silver deposit are: it is resistant to dissolution and it can withstand the attack of the oxidizing agents. In the present research, silver loaded nitrogen-doped TiO_2 (Ag–$TiO_{2-x}N_x$) was prepared using nitrogen doped TiO_2 ($TiO_{2-x}N_x$) followed by Ag loading using $AgNO_3$ by photoreduction method. Electrons can be transferred from TiO_2 to Ag deposit because of the difference in the work function of the two materials. It is approximately 4.7 eV for Ag versus 4.6 eV for TiO_2. The mechanism of this electron transfer especially from $TiO_{2-x}N_x$ to Ag is less attempted. Fang et al., had prepared TiON thin film with ultrafine Ag_2O semiconductor nanoparticles by ion beam assisted deposition and they have shown the extension of response to visible light but this catalyst was not attempted for

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photocatalysis [14]. Sun et al., reported the enhanced photocatalytic disinfection of *E. coli* by TiON/Ag_2O and they attributed the photocatalytic response of TiON matrix and Ag_2O nanoparticles not to the Ag addition itself. The optimized Ag modification concentration is determined at Ag:Ti molar ratio of 1:50 [15]. Though such studies are available in literature for Au and Pt, fewer attempts is made for the deposition of Ag [13,16–20]. The nitrogen dopant concentration was optimized for 0.15 at.% which shows better photocatalytic activity as reported earlier [21]. Smaller metal deposits are more effective than larger deposits due to the high surface area to volume ratio. Therefore the loaded amount of silver deposit is optimized at 0.05% in this study. The photocatalytic activities of these catalysts were evaluated by using phenol (Ph) as the model compound under UV/visible light irradiation. The photocatalytic efficiency of Ag–$TiO_{2-x}N_x$ is compared with $TiO_{2-x}N_x$, Ag–TiO_2 and sol gel-TiO_2 (SG-TiO_2). The synergistic mechanism of nitrogen doping and Ag loading in enhancing the visible-light photocatalytic activity of TiO_2 is studied.

2. Experimental

2.1. Materials

Titanium (IV) chloride ($TiCl_4 \geq 99.9\%$) is obtained from Merck chemicals limited, urea (NH_2CONH_2), phenol (C_6H_5OH), ammonium persulphate (APS), hydrogen peroxide (HP) (50%, w/v) and $AgNO_3$ were from Sisco-chemical Industries, Bombay. Double distilled water is used through out the experiment.

2.2. Catalyst preparation

Anatase SG-TiO_2 was prepared by sol–gel method by the hydrolysis of $TiCl_4$ as reported earlier [22]. A stoichiometric volume of the urea solution (1.5 ml of 6 g of urea in 100 ml) was added to the calculated amount of TiO_2 (1 g) to get the dopant concentration of 0.15 at.% [21]. This mixture is grinded in a mortar and dried in an oven at 120 °C for 1 h. The process of grinding is repeated for four times and the powder is finally calcined at 550 °C for 5 h. $TiO_{2-x}N_x$ powder is pale yellow in colour. Substituting nitrogen at the oxygen lattice site in TiO_2 can not proceed spontaneously, due to the existence of free energy barriers for a nitriding reaction at room temperature. But this can be over come through the enhancement of the free energy of the system by the grinding process. The free energy of the system is lowered by converting mechanical energy of grinding into distortion energy leading to the deformation, producing stress and strains which creates lattice distortion along with the creation of the several defects inside TiO_2 lattice. These oxygen defects produce high lattice distortion energy and they also increase the surface energy thereby decreasing the activation energy for the diffusion of nitrogen leading to the nitriding reaction to generate $TiO_{2-x}N_x$ [21]. Silver was deposited on the surface of $TiO_{2-x}N_x/TiO_2$ by the photoreduction of $AgNO_3$ in the presence of oxalic acid in an aqueous suspension as prepared by Szabo-Bardos et al. [23]. An aqueous solution of $AgNO_3$ (2×10^{-4} M), oxalic acid (5×10^{-3} M) along with $TiO_{2-x}N_x$/SG-TiO_2 (1 g) were added to 1 l of distilled water and it is stirred vigorously. The pH of the suspension was adjusted to 6.8–7.0 by the addition of 0.1 N NaOH solution and the suspension is irradiated with UV-light for 40–50 min. After the irradiation the solution containing Ag–$TiO_{2-x}N_x$/Ag–TiO_2 was then allowed to stand for 6 h. The colour of the reaction mixture changed from white to violet-brown under UV-light on reduction of Ag^+ to Ag^0 indicating the deposition of Ag^0 on $TiO_{2-x}N_x/TiO_2$. The pale brown solid is filtered, washed, dried and heated at 120 °C for 2 h and the colour of the solid changes to pale pink confirming the deposition of Ag. The absence of silver in the aliquot sample of reaction mixture confirms the complete deposition of noble metal on the semiconductor particles giving 0.05% deposition.

2.3. Characterization of the catalyst

The powder X-ray diffraction (PXRD) patterns were obtained using Philips pw/1050/70/76 X-ray diffractometer. FT-IR spectra were obtained using NICOLLET IMPACT 400 D FTIR spectrometer. The Diffuse Reflectance Spectra (DRS) of the photocatalysts were obtained using Schimadzu -UV 3101 PC UV-VIS-NIR UV-visible spectrophotometer. Photoluminescence (PL) spectra of the generated 2-hydroxyterephthalic acid were measured on a Hitachi F-7000 fluorescence spectrophotometer. Surface morphology was analyzed by SEM analysis using JSM840. An electron microprobe is used in the EDX mode. The specific surface area of the powders were measured by dynamic Brunner–Emmet–Teller (BET) method in which N_2 gas was adsorbed at 77 K using Digisorb 2006 surface area, pore volume analyzer by the multipoint BET adsorption system (Nova Quanta Chrome Corporation instrument).

2.4. Photochemical reactor and photonic efficiency (Φ_λ)

Experiments were carried out at room temperature using a circular glass reactor whose surface area is 176.6 cm^2. 125 W medium pressure mercury vapor lamp is used as the UV light source. Photon flux was found to be 7.75 mW/cm^2 by ferrioxalate actinometry whose wavelength peaks around 370 nm. The irradiation was carried out by direct focusing the light into the reaction mixture in open air condition at a distance of 29 cm. The reaction mixture was continuously stirred. All the experiments were performed using distilled water. Solar light experiments were performed under sunlight directly between 11 am to 2 pm when the solar intensity fluctuations are minimal and the sunrays are not oblique. The experiments were conducted in the months of April–May at Bangalore, India. The latitude and longitude are 12.58 N and 77.38 E, respectively. The average solar intensity was found to be 0.753 $kW\,m^{-2}$ (using solar radiometer). The intensity of the solar light was concentrated by using a convex lens and the reaction mixture was exposed to this concentrated sunlight. The solar radiation as a function of wavelength was measured by photometer, which shows a maximum at 450 nm. To compare the photocatalytic activity of all the catalysts, the experiments were simultaneously conducted to avoid the error arising due to the fluctuations in solar intensity. A typical experiment contains 10 mg/L of Ph solution along with 160 mg/L of the photocatalyst. The reaction mixture (250 ml) was stirred vigorously using magnetic stirrer for the entire time span of the experiment. The samples were centrifuged and filtered through 0.45 μm Millipore filter to remove the catalyst particles for the spectrophotometric analysis. The UV-Vis Spectrophotometer was used for the determination of residual concentration of the phenol in the wavelength range of 190–600 nm.

The photonic efficiencies were calculated by the method proposed by Tsoukleris et al. [24]. The photonic efficiency (Φ_λ) describes the rate of degradation of phenol molecule M_t with respect to the total rate of photons (L) incident on the reactor.

$$\Theta\lambda = \frac{M_t}{L} \tag{1}$$

The number of pollutant molecules decomposing in time '*t*' is given by

$$M_t = \left(\frac{4}{1000}\right) C_0 N(1 - e^{-kt}) \tag{2}$$

where C_0 is the initial concentration of the pollutant, N is Avogadro's number and k is the apparent first-order reaction rate constant.