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Hydrothermal synthesis of nanosized (Fe, Co, Ni)-TiO_2 for enhanced visible light photosensitive applications

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ABSTRACT

Nanosized TiO_2 and various transition metal ions (Fe, Co and Ni) doped TiO_2 were prepared through hydrothermal method. Thermal analysis confirms the formation of crystalline TiO_2. The powder X-ray diffraction patterns of all the materials show crystalline anatase TiO_2 with crystallite size in the range of 22–23 nm. Raman spectra show respective modes corresponding to anatase TiO_2 and also it coincides with the XRD data. The DR UV–vis spectra of 0.01 (Fe-, Co-, Ni)-TiO_2 extends to the visible region (450–650 nm). The extended absorbance of these materials into the visible region provides enhanced photosensitive applications under sunlight. The degradation rate of Methylene blue (MB) was used to evaluate the photosensitive activity under visible light irradiation. Results suggest that 0.01Fe-TiO_2, 0.01Co-TiO_2 and 0.01Ni-TiO_2 materials can potential be used for the generation of future fuel hydrogen by water splitting using solar radiation.

1. Introduction

In the development of new photosensitive materials, most of the investigations have focused on TiO_2, which shows relatively high activity and chemical stability under UV light irradiation [1–3]. TiO_2 is an important transition metal oxide with a major application in the area of photo catalysis, where it shows high efficiency in the removal of impurities from air, water, etc. and it can easily oxidize organic compounds [4,5]. TiO_2 is similar to that of a semiconductor with conduction band (CB) and valance band (VB) [6]. The major drawback of TiO_2 is its less activity in visible region because of its wide band gap (3.2 eV). Solar energy consists of visible light mostly (45%) and only 5% is about UV rays. Investigations are carried out to overcome this situation, providing the maximum utilization of solar energy. There is an urgent need to develop photo sensitive materials that can yield high activity under visible light irradiation by modifying TiO_2 or using other semiconductor materials. Methods such as dye sensitization, anionic and cationic doping etc. can be applied to reduce the band gap of TiO_2. In anionic, doping of nitrogen on TiO_2 has the ability to simultaneously increase the photocatalytic efficiency of TiO_2 under both Ultraviolet (UV) and visible light irradiation [7]. Doping with foreign elements will lower the band gap and help to improve the utilization of sunlight by TiO_2. In addition with this, the electron-hole recombination will be suppressed by the foreign element or metal ion incorporation [8,9]. Thus doping of TiO_2 is a promising route to extend the optical absorption to

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the visible spectral region [10]. The incorporation of transition metal ion into TiO_2 lattice is an important method to induce visible light photocatalytic activity. Here doping means replacement with a foreign element at a crystal lattice point of host material. The host material for doping is already fixed as TiO_2. On doping the colorless TiO_2 became colored because of the color of foreign element. It was observed that cationic doping in TiO_2 leads to decrease in band gap energy and enhancement of photo-activity upon sunlight [11]. Photocatalytic efficiency of TM doped TiO_2 is explained by the formation of new energy level in the band gap of TiO_2 by the dispersion of metal nano particles in the matrix of TiO_2 [12,13]. Hydrothermal method is one of the unique methods for synthesizing nanosized materials with high purity, narrow particle size distribution, controlled morphology and very high crystallinity [14].

The photosensitive efficiency of these materials was studied towards methylene blue (MB) dye degradation under visible irradiation. MB is a common redox dye mainly utilized in many industrial productions [15]. In the present study, TiO_2 and Fe, Co and Ni doped TiO_2 were prepared by facile hydrothermal method. The surface and catalytic properties were characterized by various instrumental techniques. The kinetic study and catalytic degradation of methylene blue have also been demonstrated in detail.

2. Experimental

2.1. Preparation of materials

Titanium (IV) butoxide [Ti $(OC_4H_9)_4$, TBO, (AR, Sigma Aldrich)] was used as the titania precursor. Other chemicals used were Fe $(NO_3)_3 \cdot 9H_2O$ (Merck), Co $(NO_3)_2 \cdot 6H_2O$ (Merck) and Ni $(NO_3)_2 \cdot 6H_2O$ (Merck) and ammonia solution (25%, Merck). All the chemicals were used as received.

TBO was hydrolyzed using dH_2O and adjusted the pH to basic with ammonia solution in the ratio TBO:NH_3:dH_2O (1:0.1:100). This was transferred into a Teflon lined autoclave and placed in an oven at 393 K for 24 h. The white precipitate obtained was centrifuged, dried at 343 K to get TiO_2. The same procedure was followed for the preparation of 0.01 mol% of Fe, Co and Ni doped TiO_2 with the addition of required amount of corresponding metal nitrate salts.

2.2. Materials characterization

The crystal structure of the prepared materials was obtained by X-Ray diffraction (XRD; AXS Bruker D5005 X-ray diffractometer) with CuKα radiation and calculated the crystallite size using Scherrer equation. The BET surface area and pore volume measurements were carried out at liquid N_2 temperature on BET surface area analyzer (Rubotherm, USA). The Raman spectra of the materials were recorded on a Raman spectrometer (DSR Raman microscope). The band gap energies of TiO_2 and doped TiO_2 were calculated using the absorbance data obtained from DR UV–vis spectroscopic (JASCO UV–vis spectrophotometer V550 ISV469) analysis and thereby plotting Tauc's relation $\{(\alpha h\nu) = c\,(h\nu - E_g)^n$.

2.3. Photosensitive studies

The photosensitive activity of the prepared materials was studied using Methylene blue (MB) as a model dye in an immersion type photoreactor (Heber Scientific, HIPR-COMPACT-MP-8/125/250/400) at room temperature. In a typical procedure, the material (0.1 g) was added into the aqueous MB solution (0.01 M) to form a suspension and it was added into the reactor and magnetically stirred for about 30 min in order to reach the adsorption equilibrium [16]. Before irradiation, a small amount of the solution was collected and is taken as the initial/zero hour concentration. After 30 min of stirring, the MB solution was irradiated with visible lamp (Tungsten halogen lamp, 300 W, visible, 230 V, AC, 50 Hz). About 2 mL of the reaction solution was withdrawn at particular intervals. The degradation of MB was monitored by measuring the absorbance of the solution on UV–vis spectrophotometer (PerkinElmer-USA model Lambda 35) at 665 nm in cuvette with deionised water as reference.

3. Results and discussion

3.1. Material characterization

Fig. 1 depicts XRD patterns of TiO_2 and Fe-, Co- and Ni-(TiO_2). The pattern of TiO_2 and doped TiO_2 shows well–resolved characteristic features of (101), (004), (200), (211) and (204) diffraction peaks indicating the presence of well crystalline anatase phase in the hydrothermally prepared materials. No additional peaks corresponding to the dopants were observed providing those dopants are successfully incorporated onto TiO_2 lattice or may be due to the low concentration limit to be observed in XRD [14]. The crystallite size of TiO_2 is calculated using Scherrer equation and is found to be in the range of 20–23 nm.

The specific surface area (S_{BET}) and average particle size were measured using BET is presented in Table 1.

The TiO_2 prepared through hydrothermal method has S_{BET} of 125.3 $m^2\,g^{-1}$ with an average particle size of 12.6 nm. Upon doping with the transition metals, the surface area found to be reduced and is more with 0.01Ni-TiO_2 (65.4 $m^2\,g^{-1}$). decrease