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Original Research Paper

Understanding the morphological effects of WO_3 photocatalysts for the degradation of organic pollutants

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ABSTRACT

Dimension and morphology of photocatalysts has extensive interest in order to use the effective concurrence of photon. Despite TiO_2 and ZnO, WO_3 has also been considered as a promising candidate in terms of remediation and purification that owes to its visible light absorption and non-toxic environmental friendliness. In this study, we report the preparation of nanostructured WO_3 with different morphologies for the photocatalytic degradation of organic pollutants without the presence of any sacrificial agents. The study envisages the effect of the aspect ratio of WO_3 particles on the photochemical process and their inherent reactive species mechanism. Mechanistic reasoning revealed that, apart from the hole and hydroxyl radicals as the participating species in both structures, a significant contribution from superoxide radicals takes place in the presence of nanorods and promotes the photochemical reaction. High aspect ratio facilitates the absorption coefficient and resultant efficiency. Both the catalysts retain its reactivity after regeneration and confirms the consistent catalytic reusability. Reactivity enhancement of any photocatalyst is possible through tuning the inherent structure of the material.

1. Introduction

Nanoscale building blocks are the pre-requisite for self-assembly of any scalable functional nano-/micro-materials [1]. The strong correlation between these nano-building blocks and their properties is of prime importance because of their difference in surface activity affecting the physical and chemical properties of these nanomaterials [2]. Well-controlled stable nanostructures have been mostly designed via colloidal synthesis routes using different precursors that attract immense research interest due to technological application in diverse fields [3]. Earlier, the shape independence was attributed to dominant surface properties through electronic relaxation. Later, researchers comprehended that one-dimensional structures exhibit a polarized emission linearly along the elongated axis. The past few decades has dealt with the global environmental issues that include harmful dye pollutants [4]. In order to comply with the increasing international environmental standards, the scientific advancements have been attempted for removal of such systems from the environment [5]. The most renowned photocatalyst TiO_2 has been widely studied but the relatively low quantum yield and ultra-violet absorption holds back its extensive utility in several areas [6]. However, tailoring of TiO_2 has been complied to develop new materials [7–10]. The technologically 'green' photocatalytic oxidation for the degradation of dye pollutants has revived popularity [11,12].

Thus, non-titania based semiconductor materials for visible light photodegradation of organic pollutants have gained considerable attention [13,14]. Tungsten trioxide (WO_3) is a well-known semiconducting material explored in the field of energy-based electrochromic devices, sensors and photocatalysis [15–17]. WO_3 is a prospective candidate as a photocatalyst, because of its exceptional properties such as excellent solar absorption capacity due to its small band gap that allows absorption of visible light, is chemically inert, have good thermal stability and also exhibit good photostability [18–20]. Another major advantage of WO_3 over other materials is its valence band edge position, which is more positive than H_2O/O_2 oxidation potential, and thus favorable for photo-oxidation of a wide range of organic pollutants [21–23].

Literature reports exploitation of WO_3 photocatalyst for the oxidative decomposition of organic pollutants, photoinduced hydrophilicity, organic synthesis and also electrochemical gas sensor devices [18,24–27]. The recent work includes growth of hydrates of tungsten trioxide hydrothermally onto fluorine doped tin oxide (FTO) substrate using different capping agents. The films

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grown using CH_3COONH_4 capping agent generated high photocurrents for the oxidation of methanol and also highest photoconversion efficiency was achieved under simulated solar light for water splitting [28]. Another work demonstrates the formation of hexagonal WO_3 nanoflowers and nanoblocks via microwave-assisted hydrothermal synthesis route onto FTO substrate. Flower like-WO_3 electrode showed enhanced photoelectrochemical performance in comparison to the nanoblock WO_3 coated FTO electrode [29]. Many of the studies have been carried out for the processing of the coated electrodes where the problem relies on catalyst quantification. Although hydrothermal method is an efficient methodology to synthesize nanostructures, the major lacunae in this technique are its long duration and temperature sensitivity to form nanostructures. Formation of WO_3 by solution precipitation has been used for thin film preparation for gas sensing applications [30–32]. However, different nanostructures via solution-precipitation method has not been reported so far.

In this paper, we illustrated a simple two-step process to develop WO_3 nanoparticles and nanorods by solution precipitation method. Moreover, the formation mechanism of both the WO_3 nanostructures has been discussed. The photocatalytic behaviors of these structures are evaluated towards the degradation of Rhodamine B (RB), as a model of organic pollutant, under the visible light irradiation. Scavenging experiments inputs some significant insights into the catalytic mechanism based on the morphologies of WO_3.

2. Materials and methods

2.1. Synthesis of WO_3 nanoparticles and nanorods

A simple solution precipitation method was employed to synthesize nanoparticles and nanorods of WO_3 as mentioned elsewhere [33]. The typical synthesis of WO_3 nanoparticle includes reaction of hydrogen peroxide with the preheated solid tungstic acid powder at 90 ± 5 °C. Simultaneously concentrated nitric acid was added to the reaction mixture (maintaining pH ~ 1) which undergoes an acid catalyzed exothermic reaction producing a pale greenish yellow precipitate. Isolation of the precipitated product was carried out by centrifuging the precipitate at 14,000 rpm and freeze drying the centrifuged precipitate at −52 °C with a vacuum of 20 torr. Flash calcination of this freeze dried powder at 500 °C for 5 min produces a yellow color powder of WO_3. Flash calcination is the isothermal heating of the powder (sample in alumina crucible) which is directly kept in a preheated muffle furnace for pre-requisite time and cooling of the crucible to obtain the final product.

Similar solution precipitation method has been followed to synthesize nanorods of tungsten trioxide. However, this process includes different base precursor namely, sodium tungstate dihydrate as tungsten source and cetyl-trimethyl ammonium bromide (CTAB) as structure directing reagent. Both the source and directing reagents were mixed to form a clear transparent solution which was acidified slowly using concentrated HCl to maintain pH of ~2–3 under constant stirring. Upon acidification, precipitation of the solution takes place and the reaction mixture was allowed to undergo stirring for up to 3 h to ensure complete precipitation. The process for isolation of the product was similar to the one mentioned for synthesis of WO_3 nanoparticles and also the dried powder was calcined at same temperature for same time. The final powders obtained after calcination were subjected for analytical characterizations for purity analysis.

2.2. Characterizations

The powder X-ray diffraction of the as-synthesized WO_3 nanoparticles and nanorods were measured using Rigaku diffractometer with Cu K_α radiation (λ = 0.15406 nm) to understand the crystal structures. Field emission scanning electron microscopy of the synthesized nanopowders were imaged using NOVA NANOSEM FEI450 system. On a double sided carbon tape attached to SEM stub, the powders were sprinkled, blowed to remove extra powder and sputter coated with gold for 120 s for imaging. The detailed morphological studies of the WO_3 nanoparticles and nanorods were carried out using transmission electron microscopy (TEM) on JEOL JEM-2100 TEM system. TEM samples were prepared by dispersing the powder specimens in isopropanol followed by ultrasonication for 30 min. The dispersion was drop-casted onto Cu-grid and dried under room temperature to avoid aggregation of particles followed by desiccating under vacuum for 24 h. The specific surface area of the powder specimens was measured using Quantachrome Autosorb BET apparatus, USA in the presence of nitrogen as adsorbate. The UV-diffuse reflectance measurement was carried out in Shimadzu spectrophotometer UV-2450 in the wavelength window of 200–700 nm using barium sulphate as reference. X-ray photoelectron spectroscopy measurements were carried out on a ESCA+, (Omicron nanotechnology, Oxford Instrument Germany) equipped with monochromator Aluminum Source (Al k_α radiation hυ = 1486.7 eV). FT-IR spectral measurement of the samples were carried out taking KBr as reference for the pellets.

2.3. Photochemical experiments

The visible light photocatalytic experiments were carried out in the presence of 400 W metal halide lamp procured from Halonix, India with light intensity ~86,800 lx. The metal halide lamp was jacketed with a quartz tube which was connected to chiller with continuous supply of water to ensure reaction not effected by the heat generated from the lamp and maintains room temperature for the reaction container. Rhodamine B (RB), a xanthene fluorene cationic dye, was chosen as a model dye pollutant for photochemical degradation process using WO_3 nanoparticles and nanorods. A standard stock solution of 20 mg/L was prepared for Rhodamine B and maintained for all the catalytic reactions. The photochemical reactions were conducted at its natural pH to avoid the effect of externally added cations and anions in the reaction. The concentration of catalyst was maintained at 1 g/L for photochemical reactions. In the typical photochemical process, 50 ml of Rhodamine B solution with 50 mg catalyst was taken into a quartz beaker and the suspension was stirred magnetically during the photochemical reaction in the presence of light irradiation. Prior to each of the catalytic reaction, the reaction suspension containing dye and catalyst was kept in dark under constant stirring to ensure adsorption-desorption equilibrium. Few ml of mixed solution was sampled at certain time intervals, and centrifuged to separate the catalyst and dye solution. The dye solution was evaluated for its concentration using UV–Vis spectrophotometer by measuring the absorbance characteristic wavelength of the dye. The experiments were conducted in triplicates and the experimental error was less than ±3% in the time resolved degradation profile. Scavenging experiments were carried out with 1 mM of scavengers in the reaction solution.

3. Results and discussions

3.1. Powder X-ray diffraction

The crystal phase and purity of the as-synthesized WO_3 nanopowders were identified using the powder X-ray diffraction (XRD) measurement. Fig. 1a shows the XRD pattern of both the WO_3 nanoparticles and nanorods. The XRD results depict that both the patterns are in good agreement with the standard data of the

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