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Enhanced photocatalytic activity of V_2O_5 nanorods for the photodegradation of organic dyes: A detailed understanding of the mechanism and their antibacterial activity

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ABSTRACT

Photocatalytic activity of the hydrothermally prepared V_2O_5 nanorods had been tested for Rhodamine 6G (Rh-6G), methyl orange (MO) and methylene blue (MB) under visible light irradiation. The photodegradation was maximum for Rh-6G (85%) followed by 48% and 24% for MO and MB respectively and it was faster in Rh-6G. The degradation rate constant and half-life time were 0.603 h^{-1} and 1.229 h respectively for Rh-6G and responsible for enhanced photocatalytic performance. The degradation of Rh-6G had occurred via N-de-ethylation process. The Rh-6G had best performed in the neutral pH conditions, better in acidic and poor in basic conditions. Increasing photodegradation in Rh-6G was understood by scavenging the increasingly formed $^{\bullet}OH$ radicals by the PL emission of formed photoluminescent species 2-TAOH. The effect of active $^{\bullet}O_2^-$ is demonstrated to be major player on the degradation of Rh-6G. The V_2O_5 nanorods showed reproducible, repeatable, and efficient degradation of Rh-6G in aqueous solution. Additionally, it showed good anti-bacterial activity against *Escherichia coli* and *Staphylococcus aureus* bacteria.

1. Introduction

Environmental pollution is the furthermost problems in recent years especially water pollution. Discharge from textile industries is a big threat to it by having various organic dyes (*e.g.*, rhodamine-6G (Rh-6G), methyl orange (MO) and methylene blue (MB)) in the usable water. Organic dyes are harmful, potentially carcinogenic, and non-biodegradable, cause serious threat to environment as well as to human health. The photocatalytic degradation is a significant process of waste water treatment and has the ability to remove harmful heavy organic contaminations. This (photocatalysis) can absolutely decompose organic dyes into CO_2 and H_2O. It has several advantages like fast, non-destructive, inexpensive, complete mineralization and low temperature process. This method of photodegradation requires a photocatalyst with appropriate properties such as "optimum band gap in the visible range, lower recombination of photogenerated electron-hole pairs, long-term stability, high catalytic activity, low-cost preparation, high surface area, chemical inertness and strong oxidizing capacity in order to degrade organic compounds" [1]. Recently, metal-oxide photocatalysts have been researched a lot due to their properties such as nontoxic, harmless, excellent photocatalytic and antibacterial activities [2–4]. Many of them show side effects such as causing diseases, bacterial or fungal infectivity in the solution. In order to avoid them, several antibacterial and antifungal agents are also generally used for the public healthiness issues [5]. Therefore, new type of materials with dual activity such as photocatalysis and antibacterial are highly welcome in this field. In order to have improved photocatalytic and antibacterial/antifungal properties, the good choice is the class of nanomaterials because their performance depends on size, shape, structure and surface properties and moreover they are tunable [6]. While many different metal-oxide photocatalysts have been used for dye degradation [7,8], their activity had mainly been limited to ultraviolet-light owing to their large band gap values. Therefore, improvement of visible-light active photocatalysts has become necessary and active research is required on it [9]. In addition, mixed-metal vanadates have also been researched due to their smaller bandgap values and active photocatalytic degradation under visible-light. For example, $BiVO_4$ [10] and Ag_3VO_4 [11] were used as photocatalyst for MB dye degradation and water splitting under

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visible light irradiation [12]. Among various photocatalysts, V_2O_5 is a promising *n*-type semiconducting material for photocatalytic degradation applications due to its narrow band gap (of approximately 2.4–2.8 eV), non-toxicity, good chemical stability, photo stability, and high visible light absorption [13,14]. That too, there is a growing interest in using V_2O_5 in the form of nanostructured materials because, desired size and morphology make them remarkable in many applications. Specifically, nanostructured one-dimensional (1D) materials such as nanotubes, nanorods, nanobelts and nanorods have got much attention due to their distinct geometry, new physical and chemical properties and applications in numerous areas [15–18].

This work presents the preparation of V_2O_5 with nanorod morphology by hydrothermal method and their characteristic properties. Hydrothermal method was used in the synthesis, in particular, to fabricate the 1-D nanostructures because of its low critical temperature and pressure, and scalability. The same method was used to prepare V_2O_5 nanoribbons [19], nanowires [20], nanoparticles [21], nanobelts [22], nanorods and nanosheets [23] etc. In most of the preparations, the hydrothermal method was used with either surfactants or templates in order to control the shape, size or morphology of the nanostructures. In this work, the hydrothermal method was used without surfactants/templates but with relatively lower working temperature (120 °C). Photocatalytic degradation of the orthorhombic V_2O_5 nanorods was investigated under visible light irradiation for the degradation of Rh-6G, MB and MO dyes in an aqueous solution. Among various organic dyes, the Rh-6G is a recalcitrant textile dye and heavily used as coloring agent for wool, cotton, silk and paper. Despite being used in textile industry, it (Rh-6G) is non-volatile, highly water soluble, tending to cause cancer, inducing mutation and teratogenicity in human body and it causes severe damage to retinal ganglion cells [24]. Thus it can direct to critical environmental and health hazard. And hence, these toxic effluents are required to be treated properly before getting mixed in the normal water bodies. Therefore, finding a suitable photocatalyst that can work against Rh-6G has got significance and taken up in this research. In addition to these, the performance of the V_2O_5 photocatalysts in the photodegradation of MO and MB is also reported.

2. Experimental

2.1. Preparation of V_2O_5 nanorods

All the precursor chemicals used were purchased from Himedia Chemicals Company, India and used as-received without any additional purification. In a typical synthesis of V_2O_5 nanorods, 0.1 M ammonium metavanadate (NH_4VO_3) was dissolved in 80 ml of distilled water which formed a pale yellow solution. Diluted sulfuric acid (H_2SO_4/H_2O = 1:4 v/v) was added drop-wise into the above solution until the pH reaches to 3. Finally the solution had become orange and that was transferred into a Teflon-lined stainless steel autoclave and kept at 120 °C for 24 h and then naturally cooled down to room temperature. The product was centrifuged with distilled water and absolute alcohol and then dried at 70 °C under vacuum. The as-prepared sample was heat-treated at 500 °C for 1 h in air and the final yellow color powder used for this study.

2.2. Characterization

Thermal characteristics of the nanorods was studied by thermogravimetric analysis (Q600 SDT, TA Instruments) carried out at a heating rate of 10 °C/min in air atmosphere. X-ray diffraction (XRD) studies were carried out in a powder X-ray diffractometer (Ultima-IV, Rigaku) with Cu-k_α radiation at a scan speed of 0.02°/s. Structural phase analysis through Rietveld refinement was performed by using GSAS-EXPGUI software package. Microstructure was studied by Scanning Electron Microscope (Hitachi, S-3400N) operated at 30 kV and Transmission Electron Microscope (TEM-JEOL 2010). The TEM was operated at 200 kV with a LaB_6 electron source and equipped with XEDS (x-ray energy dispersive spectroscopy) detector. Composition analysis was carried out by XEDS carried out in the same SEM microscope. The UV–vis absorption spectra were acquired in the spectrophotometer (Varian, Model: 5000) in the wavelength range from 200 to 600 nm with a resolution of 1 nm. The slit width used was 1 nm and 8 nm for powder and liquid samples respectively. The light source used was a xenon lamp. Photoluminescence (PL) spectra were carried out in a spectroflurometer FLUOROLOG-FL3-11 (Horiba) with an excitation wavelength, λ_{ex} = 226 nm with slit width of 4 nm. Fourier transform infrared (FTIR) spectra were recorded in the 4000–400 cm^{-1} range by using ThermoNicolet Model: 6700 with KBr pellet method. Time Resolved Photoluminescence Lifetime (TRPL) measurement was carried out in a spectroflurometer FLUOROLOG-FL3-111 (Horiba-Jobin-Yvon) with an excitation wavelength, λ_{ex} = 295 nm from LED source with a slit width of 4 nm. Brunauer-Emmett-Teller (BET) specific surface area measurements were carried out in Micrometrics Gemini VII 2390 by using N_2 absorption at 77 K.

2.3. Analysis of the intermediate products of photocatalysis

The photodegradation pathway products of Rh-6G dye under visible light irradiation was studied by using electro spray ionization mass spectra (ESI-MS) experiments (6530 B Agilent Q-TOF LC/MS). The analysis was carried out with capillary voltage of 3500 V, Frag mentor voltage of 175 V, gas temperature of 300 °C and syringe rate of 0.1 μl/min respectively.

2.4. Photocatalytic degradation experiment

The photo-induced degradation of the model dye Rh-6G in aqueous solution by the photocatalyst V_2O_5 nanorods was evaluated at room temperature after exposed to visible light irradiation. For the photodegradation experiment, a 20 mg of the photocatalyst (V_2O_5) was dispersed in 100 ml of Rh-6G solution with a concentration of 5×10^{-5} M. The mixture of Rh-6G aqueous solution and V_2O_5 was kept in dark for 30 min to achieve the establishment of adsorption-desorption equilibrium of Rh-6G on the surface of V_2O_5. Then the solution was irradiated continuously with visible light for 5 h, and every 30 min of irradiation, 3 ml of the irradiated solution was collected and their absorption spectra were recorded. Quantitative determination of Rh-6G photodegradation was obtained from their absorption spectra. Similar photodegradation experiments were carried out on MB and MO.

2.5. Trapping experiment

The radical trapping experiments were carried out in order to identify the active species that are produced during photocatalysis and involved actively in photodegradation of the dye. The compounds such as benzoquinone (BQ) and Tert-butyl alcohol (TBA) were used as scavengers to trap the active species such as superoxide radical ($^{\bullet}O_2^-$) and hydroxyl radical ($^{\bullet}OH$) respectively. The concentrations of the solutions were prepared with 1 mM and 0.1 mM of BQ and TBA respectively and then added into the 100 ml of the photocatalytic reaction solution. Then the solution was irradiated with visible light and at every 30 min aliquots of the solution was withdrawn and their UV spectra were measured.

2.6. Antibacterial activity

Antibacterial activity of V_2O_5 nanorods was tested against *Escherichia coli* (Gram negative) and *Staphylococcus aureus* (Gram positive) bacteria by Agar well diffusion method described in the literature [25]. The tryptone glucose yeast extract (TGYE) agar was used for antimicrobial activity assay. The indicator organisms such as *E. coli* and *S. aureus* were procured from microbial type culture collection centre