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Visible light driven photocatalysis and antibacterial activity of $AgVO_3$ and $Ag/AgVO_3$ nanowires

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ABSTRACT

$Ag/AgVO_3$ nanowires and $AgVO_3$ nanorods were synthesized in aqueous media via a facile sonochemical route. The as-synthesized products were characterized by X-ray diffraction, Brunauer–Emmett–Teller surface area analysis, scanning electron microscopy together with an energy dispersion X-ray spectrum analysis, transmission electron microscopy and UV–vis diffuse reflectance spectroscopy. The results revealed that inert atmosphere promotes the formation of $Ag/AgVO_3$ nanowires. The photocatalytic studies revealed that the $Ag/AgVO_3$ nanowires exhibited complete photocatalytic degradation of Rhodamine B within 45 min under visible light irradiation. The antibacterial activity of $Ag/AgVO_3$ nanowires was tested against *Escherechia coli* and *Bacillus subtilis*. The minimum growth inhibitory concentration value was found to be 50 and 10 folds lower than for the antibiotic ciprofloxacin for *E. coli* and *B. subtilis*, respectively. The antibacterial properties of the β-$AgVO_3$ nanorods prove that in case of the Ag dispersed $Ag/AgVO_3$ nanowires, the enhanced antibacterial action is also due to contribution from the $AgVO_3$ support.

1. Introduction

Organic dyes find numerous applications in the industry but they are a serious source of water pollution [1]. Most of these dyes are carcinogenic and toxic and apart from being stable, they are also resistant to photo degradation, biodegradation and oxidizing agents [2]. Hence recently there is a lot of emphasis on the use of semiconductor photocatalysts for environmental purification. For photocatalytic decomposition of organic contaminants to occur, the valence band of the photocatalyst must meet the potential level of oxidation of the organic contaminants and O_2 must be involved in the photocatalytic system. The reaction of electron and holes with water or O_2 absorbed on the surface generates active oxygen radicals, which accounts for the oxidization of the organic compound. Among the various semiconducting photocatalysts, TiO_2 has emerged a frontrunner due to its reliable photocatalytic performance and outstanding chemical stability. However, TiO_2 suffers from low efficiency under visible-light illumination since it has a large bandgap of 3.2 eV. This significantly limits its photocatalytic applications since UV radiations constitute only ~4% of sunlight. Hence, a lot of research has been devoted to the development of visible-light-driven photocatalysts in order to ensure more efficient utilization of solar energy and indoor light [3–7]. One way to do this is to generate intermediate energy levels in UV-active photocatalysts by anion doping, metal doping or oxygen deficiency generation to turn them into visible-light photocatalysts. The drawback of this method is that the dopants might serve as carrier recombination centers and hence decrease the photocatalytic efficiency. The other method is to try and develop novel materials with visible light photocatalytic activity.

Among these new photocatalysts, silver vanadates, particularly Ag_3VO_4 have been demonstrated to be efficient photocatalysts under visible light irradiation, due to its narrow band gap and good crystallization [8–11]. The valence bands of silver vanadates consist of hybridized Ag $4d^{10}$ orbital and O $2p^6$ orbitals, and their conduction bands consist of hybridized Ag 5 s orbitals with V 3d orbitals. It is the hybridization of the O $2p^6$ orbitals with the completely filled $4d^{10}$ orbitals of silver ions that results in fixing the valence band at a more positive energy level than that of O $2p^6$, resulting in a narrowed band gap. Very recently, hydrothermally synthesized β-$AgVO_3$ has been shown to demonstrate photocatalytic activity under visible light irradiation [12]. Apart from photocatalytic activity, the research related to novel silver-based materials has gained a lot of impetus owing to their promising

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antibacterial activity against several microorganisms. Thiol groups present in the enzymes are involved in bacterial cell metabolism. The silver ions strongly interact with these thiol groups causing cell death [13–17]. With the advent of nanotechnology, such silver based nanomaterials also finds better use in a variety of applications including visible light-driven photocatalysts [18–21], electrochemical cells [22], cathode material in lithium batteries [23,24] and as antibacterial agents [25,26]. A primary reason for this improvement is due to the typically high surface area of nanomaterials, which provides for a large number of adsorption sites.

In this work, we report the photocatalytic and antibacterial properties of $Ag/AgVO_3$ nanowires and $AgVO_3$ nanorods synthesized using sonochemical technique. Sonochemical synthesis is based on acoustic cavitation resulting from the continuous formation, growth and implosive collapse of the bubbles in a liquid [27,28]. These nanowires show considerable photocatalytic activity, which has been studied through the degradation of rhodamine B (RhB) in an aqueous solution. Results of antibacterial tests show that this hybrid material has a promising antibacterial activity against both gram negative and gram positive bacteria strains like *Escherichia Coli* and *Bacillus subtilis*, respectively. The role played by the $AgVO_3$ support in this observed antibacterial activity has been evaluated. The findings in this study establish the multifunctionality of such sonochemically synthesized $Ag/AgVO_3$ nanowires, both as an antibacterial agent and as an efficient material for photocatalysis.

2. Experimental details

2.1. Synthesis

The reactions were carried out at room temperature under inert atmosphere (argon). High purity silver nitrate [$AgNO_3$] and ammonium metavanadate [NH_4VO_3] were obtained from commercial sources (Aldrich). AR grade ammonia solution was used. The detailed synthesis procedure was as follows: 13.5 mmol of NH_4VO_3 was dissolved in 80 ml of deionized water. Then, 13.5 mmol $AgNO_3$ was added dropwise into the above solution with stirring. The pH of the solution was adjusted to ~7 by adding ammonia solution. The system was then irradiated with high intensity (100 W/cm^2) ultrasonic radiation (Oscar Ultrasonics) operating at 40 kHz, under argon for 1 h. The titanium horn was inserted to a depth of 6 cm in the solution. After sonication, the colloidal precipitate was centrifuged and washed with deionized water. Final washing was given with ethanol and the yellowish residue obtained was air dried.

2.2. Characterization

X-ray diffraction (XRD) measurements were carried out on a Philips Instrument, operating with Cu-*K*α radiation (λ = 1.5406 Å) and employing a scan rate of 0.02°/s in the scattering angular range (2θ) of 10° to 80°. Silicon was used as an external standard for correction due to instrumental broadening. SEM micrographs were recorded using Seron Inc. make model AIS 2100 scanning electron microscope at 20 keV. The samples were prepared for SEM by putting a drop of ultrasonicated silver vanadate nanopowder dispersed in methanol over a mirror polished Si single crystal to reduce the affect of agglomeration. EDX analyses were carried out using an Inca Energy 250 instrument coupled to Vega MV2300t/40 scanning electron microscope. Conventional TEM micrographs were recorded on a Libra 120 KeV Electron Microscope (Carl Zeiss). The particulates obtained, were dispersed in methanol solution and then deposited on the carbon coated copper grids for TEM/SAED studies. The surface areas were determined by N_2 adsorption using the Brunauer–Emmett–Teller method (BET, Bel Japan Inc., Belsorp II). The diffuse reflectance spectra were determined with a UV–vis spectrophotometer (Varian Cary 5000) with $BaSO_4$ as the reference standard, and the diffuse reflectance spectra were transformed into the absorption spectra by the Kubelka–Munk method.

2.3. Photocatalytic decolorization of RhB

For photodegradation reaction, 0.03 g of the photocatalyst was added to 80 ml of RhB solution (0.02 mM) in a photoreactor quartz vessel. Before illumination, the suspensions were magnetically stirred for 1 h in the dark to ensure the establishment of an adsorption/desorption equilibrium between the silver vanadate sample and RhB. The photodegradation reactions were carried out at room temperature under visible-light irradiation from a 150-W Xe lamp ($\lambda \geq 400$ nm). The photocatalytic activity of the nano $AgVO_3$ was evaluated by photocatalytic decolorization of RhB aqueous solution by checking the absorbance at 554 nm through a UV–vis spectrophotometer (Shimadzu, UV-1650). At given irradiation time intervals, 3 ml of the suspensions were collected, centrifuged, and filtered through a Millipore filter to separate the photocatalyst particles. The percentage of degradation is recorded as C/C_0. C is the immediate concentration of the RhB at each irradiation time interval and the C_0 is starting concentration when adsorption–desorption equilibrium is achieved. In the photocatalytic stability experiments, the photocatalyst was collected by centrifugation and then redispersed in fresh RhB aqueous solution for the next cycle. Other experimental parameters were kept unchanged. In order to determine the reproducibility of all the results, at least duplicated runs were carried out for each condition for averaging the results, and the experimental error was found to be within ±2%. FTIR spectra of nano silver vanadate and RhB mixture before and after the photocatalytic reaction were recorded on a Shimadzu, IRPrestige-21 instrument.

2.4. Evaluation of antibacterial activity

The antimicrobial activity of the nanostructured silver based vanadate were investigated against two strains *E. coli* and *B. subtilis* as the representative species of gram-negative and gram-positive bacteria, respectively. The agar diffusion method was followed for antibacterial tests [29]. Petri plates were prepared by pouring 20 ml of Mueller Hinton agar and allowed to solidify for susceptibility tests against bacteria. Ciprofloxacin (2.5 μg/disc) for bacteria was used as positive control and 5% dimethyl sulfoxide (DMSO) was used as blind control in these assays. Finally, the inoculated plates were incubated at 37 °C for 24 h and the zone of inhibition was observed and measured in millimeters. Each assay in this experiment was repeated four times. The minimal inhibitory concentration (MIC) values determination were performed by microdilution in Mueller–Hinton broth in a wide concentration range of treatments, as described by the Clinical and Laboratory Standards Institute (CLSI) [30]. Initially, the bacteria were grown in Mueller–Hinton solid medium at 37 °C to obtain the isolated colonies. Subsequently, the colonies were solubilized in a saline solution 0.85% (w/v) and adjusted to the 0.5 index of the MacFarland scale (1.5×10^8 colony-forming units (cfu)/ml). This solution was diluted in Mueller–Hinton broth and distributed in a 8-well plate at a density of 10 cfu/well. Each well was treated with different concentrations of silver-based nanostructured materials. The plates were incubated for 18 h and the optical density at 595 nm was measured after this period. After the period of incubation, the tube containing the least concentration of silver vanadate nanostructures showing no visible growth was considered as MIC.