SYNTHESIS OF NANO MATERIALS BY MICROWAVE ASSISTED HYDROTHERMAL METHOD

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Abstract: Bismuth tungstate nano materials have been successfully synthesized by microwave assisted hydrothermal method. Bismuth nitrate ($Bi(NO_3)_3.5H_2O$) and sodium tungstate ($Na_2WO_4.2H_2O$) are used as a starting material for the preparation of nano materials and solution pH was maintained to 3. The prepared material was characterized by X-ray diffraction (XRD) to study the phase state, whereas surface morphology was observed by Scanning Electron Microscopy (SEM). The surface area was determined by Brunauer-Emmett-Teller (BET) method. The results revealed that materials are crystalline in nature having crystallite size of ~ 24 nm with surface area of 6.5 m^2/g. SEM image of prepared materials showed a unique discrete hierarchical morphology. The prepared material showed visible light active photocatalytic nature for the decomposition of Rhodamine B.

Keywords: Microwave Assisted Hydrothermal Method; Bismuth Tungstate (Bi2WO6); Nanocrystalline materials; Hierarchical structure; Photocatalytical activity; Rhodamine B (RhB) .

INTRODUCTION

Visible light active nanocrystalline material is a promising material for the removal of toxic substances from air and water pollution. It has been recently used as a visible light active photocatalyst for the conversion of light energy into chemical energy. Intensive efforts have been devoted to develop ecofriendly materials that are active under visible light irradiation [1].

After the discovery of Fujishima and Honda, titanium dioxide (TiO_2) was taken as a suitable photocatalyst due to its chemical inertness, long term stability and strong oxidizing abilities [2]. A number of studies on TiO_2 photocatalyst have been done by different scientists. In 1985, Matsunaga et al. studied on photochemical sterilization of microbial cells by semiconductor powders [3]. Then research further broadens the scope of semiconductor photocatalysis. Hoffman et al. have reported that UV irradiation induces superhydrophilicity in TiO_2 through the formation of surface hydroxyl groups [4]. This effect allows water droplets to run freely across a TiO_2 coated surface, and is used in products such as self-cleaning glass and anti-fogging mirrors for cars. However, it was investigated that the band gap of ultraviolet light induced materials are very large and are more active to UV irradiation which accounts for less than 4% of the sunlight irradiation that limits its uses. Similarly, in 2001, Luo et al. monitored WO_3 films anodically grown on tungstate foil substrate which were photoactive for the reduction of methylene blue [5]. Kudo and Hijii who have first discovered the use of solid-state method in the synthesis of Bi_2WO_6 photocatalyst in studies of water oxidation for oxygen liberation [6]. In 2013 Adhikari et al used microwave assisted hydrothermal method for the formation of photocatalyst. The composite photocatalyst exhibited much higher photocatalytic activities compared to other synthesis methods [1]. At present, much effort has been devoted to prepare ecofriendly materials to apply in environmental pollution remediation process and to understand its phasial state, morphology and surface area [7].

Herein, we report the preparation of bismuth tungstate nano materials by microwave assisted hydrothermal method. The prepared material was characterized by XRD, SEM, BET to find out phase state, morphology and surface area respectively. The material was then applied to decompose azo dye from water.

EXPERIMENTAL

Materials

All reagents used were of analytical grade and were obtained from Sigma Aldrich. All the solutions were prepared in distilled water. (0.1 M) Na_2WO_4 was prepared by dissolving appropriate amount of Na_2WO_4 in distilled water and (0.2 M) $Bi(NO_3)_3$ was prepared by dissolving $Bi(NO_3)_3$ in acidified distilled water (1:1 HNO_3/H_2O)

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Instrumentation

X-ray diffraction (XRD) patterns of the materials were obtained with a Rigaku X-Ray Diffractometer using monochromatized Cu Kα (λ=1.54A°). The surface morphology of the materials was studied using Scanning Electron Microscopy (SEM), mini-SEM (Nanoeye, Co) applying current of 120 mA and voltage of 30 kv. The surface area of the material was investigated by BET analyzer (micrometrics, ASAP 2020) by adsorption of liquid nitrogen for 2 hours. Photocatalytic activity of the material was performed by using Portable solar simulator (PEC-L01, pecell, Am 1.5 G) by wavelength of visible light.

Microwave Assisted Hydrothermal Method

0.1 g of the prepared material was taken in a pyrex glass cell (50 mm x 50 mm). 20 mL of (0.1 M) Na_2WO_4 and 20 mL of (0.2 M) $Bi(NO_3)_3$ was mixed in a beaker using magnetic stirrer. The pH of the solution was maintained to 5 using NH_4OH. The resulting precursor solution was transferred to Teflon lined microwave reactor. The reactor was placed in the microwave. The 50°C microwave temperature and 1 hour microwave holding time was maintained. Then after 1 hour the material was obtained. Thus obtained material was washed thoroughly with distilled water, centrifuged and dried. The material was then finally calcined at 400°C for 4 hour in an air environment.

Photocatalytical Degradation Process

The 50 mL of aqueous solution of rhodamine B (10 mg/L) was introduced into beaker and stirred to make a suspension of dye and material. The suspension was kept in dark for half an hour to achieve adsorption – desorption equilibrium. Then the suspension was kept under the simulated sun light irradiation for 180 minutes by using 150 W xenon arc lamp solar simulators to investigate photocatalytic activities. The photocatalytic activities were then examined by measuring the absorbance of the solution at every 30 minutes using UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

Phase Characterization by XRD

Fig. 1 shows the XRD pattern of the material. A sharp diffraction peaks can be clearly seen in the pattern which indicates that the prepared material is crystalline in nature. The peaks (131), (200), (202), (133), (262) and (004) at 2 theta degree are assigned for Bi_2WO_6 orthorhombic structure according to JCPDS indexed data (JCPDS No. 01-79-2381) [8].The additional peaks are not observed in XRD pattern indicating absence of any impurities. The crystallite size was estimated using Scherrer's equation D = λ, where K (0.9) is a shape factor for spherical particles, λ(0.15 nm) is the wavelength of the incident radiation of X-ray, β is the full width at half-maximum height, θ is Braggs angle and D is the crystallite size. The crystallite size of the materials was found to be 21 nm- 27 nm. Hence, the prepared material is pure crystalline nano material having average crystallite size of 24 nm.

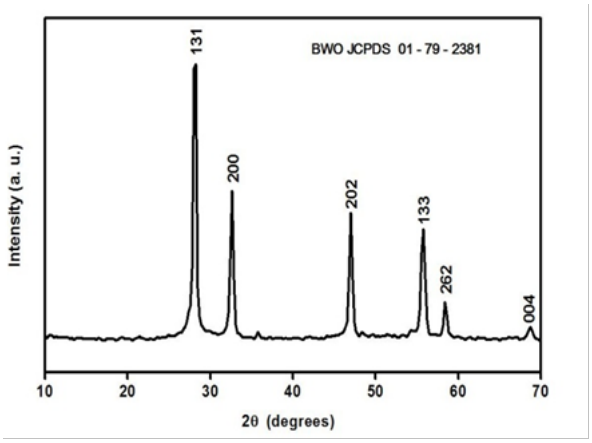

Figure 1: XRD pattern of prepared Bi_2WO_6 material.

Surface Morphology by SEM

The morphology of the nano materials was studied by Scanning Electron Microscopy. As seen from a low scanning Mini SEM image of bismuth tungstate materials (**Fig. 2)**, consists of well dispersed fine particles. The entire material showed discrete flower like hierarchical morphology.

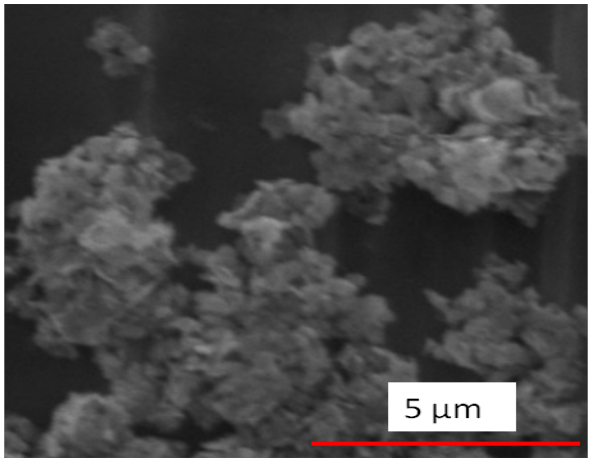

Figure 2: SEM image of prepared Bi_2WO_6 material.

Determination of Specific Surface Area by BET

The application of the materials mainly depends upon the surface morphology and specific surface area. Greater the surface area higher will be the activity of the materials. Specific surface area of as synthesized materials was found to be 6.5 m^2/g which is larger than the surface area determined by solid state reaction [9] and in agreement with the specific surface area calculated by hydrothermal method [10].

Determination of Photocatalytical Activity of the Materials

To investigate the photocatalytic activity of the prepared Bi_2WO_6 sample Rhodamine B was used as a model pollutant. The photodegradation of Rh B was carried out in presence of simulated solar light irradiation. **Fig. 3,** shows the photocatalytic degradation rate of prepared material under visible light irradiation. As can be seen from **Fig. 3,** there is a significant decrease in concentration of Rhodamine-B. Almost 80% of Rhodamine molecules are found to be decomposed. The material showed great potentiality towards photocatalytical activity. Further investigation can be done to improve the photocatalytic behavior.

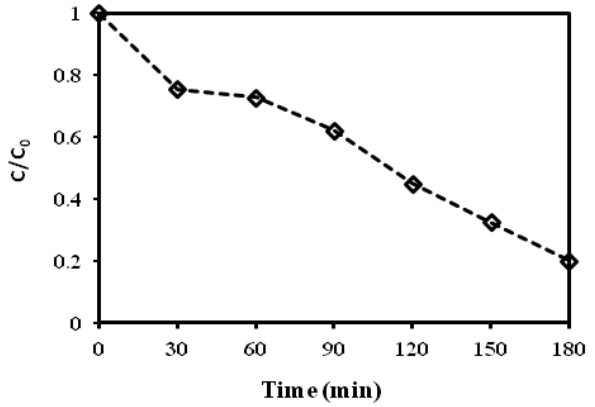

Figure 3: Photocatalytical degradation of Rhodamine B in presence of prepared Bi_2WO_6 material under simulated solar light irradiation.

CONCLUSION

The nanocrystalline Bismuth Tungstate materials have been successfully synthesized using $Bi(NO_3)_3.5H_2O$ and $Na_2WO_4.2H_2O$ as a starting material by microwave assisted hydrothermal process. The synthesized materials are in nano form having crystallite size of ~ 24 nm. The surface morphology of the synthesized bismuth tungstate was found to be flower like hierarchical structure. The specific surface area was calculated as 6.5 m^2/g. Results obtained from the photocatalytical degradation of Rhodamine B showed that as prepared bismuth tungstate is a promising material with high activity towards photocatalysis.

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