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Synthesis of Bismuth Stannate Nanoparticles with High Photocatalytic Activity under the Visible Light Irradiation

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ABSTRACT. Malachite Green is one of the most important organic dye, it contains triphenylmethane groups and it has been widely used for many industries. The hazardous dyes were rapidly act on immune and reproductive systems with carcinogenic effect of human health. Different methods were used for the hazardous removal in various industries, such as photocatalysis, biological treatment and adsorption process. The bismuth stannate nanoparticles have special properties of the hydrogen storage, biomolecule detection, gas sensors and catalysis. The bismuth stannate nanoparticles can be used for the degradation of organic pollutants and bismuth stannate is an important ternary oxide semiconductor with a wide band gap material. The composites were synthesized by a hydrothermal method, the obtained product was characterized byXRD, Raman, the morphology structure was confirmed by scanning electron microscopy and optical properties were carried out by DRS-UV-Vis spectroscopy. The excellent photocatalytic performance of the catalyst was evaluated by malachite green under the visible light.

Introduction. Bi₂Sn₂O₇ plays an important role in photocatalytic activity and different temperature stabilities in the hydrothermal reaction processes. Nowadays this pyrochlore structured material have several applications such as solar energy conversion, environmental remediation [1-2], catalysis, gas sensors [3-4] and hydrogen generation [5-6]. Many canvassers were reported to the excellent photocatalytic performance, chemical stability, low cost and non-toxicity of the semiconductors [7- 9]. The Photocatalytic degradation can be assigned for high mobility of photoinduced electrons from band dispersion and its ion separation [10].

 $Bi₂O₃$ is a p-type semiconductor material and $SnO₂$ is n-type material, were used in a many industries and several applications of Bi- based material. This material is used in anticancer activity, antimicrobial[11], electrical, optical and fast-ion conducting characteristics and as well performance of photocatalysis[12-17]. In this work, we have synthesized materials at higher temperature, which facilitates the formation of nanoflakes with uniform shape and size. Here itaconic acid can act as a surfactant in case of shape and size growth for the bismuth stannate surface. The $Bi_7Sn_{0.1}O_{10.7}$ nanoparticles have excellent photocatalytic performance for the photocatalytic degradation of malachite green dye under visible light irradiation.

Experimental methods.

 \overline{a}

Synthesis of Bi₇ Sn_{0.1} O_{10.7} nanoparticles. The Bi₇Sn_{0.1}O_{10.7} nanoparticles were synthesized by hydrothermal method. SnCl₂.2H₂O (2mM) was dissolved in methanol. Bi $(NO₃)₃5H₂O$ was

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dissolved in dilute nitric acid. The tin solution was added dropwise with continuous stirring for 2 h and small amount of itaconic acid was added to the solution Finally KOH solution was added, after this precursor were transferred to stainless steel teflon autoclave and heated at 170 ºC for 12 h. The obtained product was centrifuged at 12000 rpm immediately to get a residue. The residue is washed with ethanol and dried at a room temperature.

Characterization techniques. The morphology of synthesized samples was characterized using SEM at Hitachi S-3000H, Japan. The crystalline cubic phase of the $Bi_7Sn_{0.1}O_{10.7}$ is evaluated by using Bruker D8 ADVANCE and monochromatic Cu K α_1 radiation ($\lambda = 1.5418$ Å). DRS -UV- visible spectroscopy was carried out by Perkin Elmer (lambda 35 India PVT LTD).

Photocatalytic activity. The photocatalytic degradation of Malachite green in an aqueous solution was carried out by using $Bi_7Sn_{0.1}O_{10.7}$ materials at a room temperature. In a typical experiment, bismuth stannate (25 mg) and 100 ml MG (1×10^{-5} M) solution was sonicated for 5 min. and continuously stirred. The solution was equilibrated for 5 min. The mixture is subjected to visible light irradiation. The phodegradation was followed by collecting the solution at equal intervals, which was analysed by using UV- Visible spectroscopy.

Result and discussion.

Structural and morphological analysis using XRD and SEM. The synthesized $Bi_7Sn_{0.1}O_{10.7}$ nanoparticles structural analysis will be carried out by X-ray diffraction and the patterns were shown in Fig. 1. The bismuth stannate nanoparticle diffraction patterns corresponds to the crystalline cubic phase. The peaks at $2\theta = 27.6^{\circ}$, 31.9° , 45.8° and 54.3° corresponds to the diffraction planes (111, 200, 220 and 311) were confirmed by JCPDS no - 42-0187. Fig. 2 shows the flakes like morphology of synthesized $\text{Bi}_7\text{Sn}_{0,1}\text{O}_{10,7}$ nanoparticles with uniform size.

Fig. 1. X-Ray diffraction patterns.

Fig. 2. SEM images of Bi⁷ Sn0.1 O10.7 nanoparticles.

Raman spectroscopy. Raman spectroscopy studies of the obtained bismuth stannate nanoparticles are shown in the Fig. 3. The peak at 98 cm⁻¹ corresponds to the A_{1g} modes of metallic bismuth and 119, 312 and 445 cm⁻¹ are $Bi - O$ stretching modes of the catalyst. The modes at 147 and 532 cm⁻¹ peak was commonly according due to the O - M - O (M - Bi, Sn) bending modes of the products.

Diffuse reflectance spectroscopy. Fig. 4 shows the diffuse reflectance spectrum of the bismuth stannate nanoparticles with systematic band gaps are observed. Bi₇Sn_{0.1}O_{10.7} optical band gap energy is 3.5 eV. The band gap values are comparable with previous reports.

FT-IR Spectroscopy.

The FT-IR spectrum of as prepared bismuth stannate nanoparticles was shown in Fig. 5: These materials show three peaks at 504, 611 and 1038 cm⁻¹. Band at 504 cm⁻¹ corresponds to the Bi-O vibrations 611 and 1308 cm⁻¹ are attributed to stretching vibration of the M-O (Sn and Bi).

Fig. 3. Raman, DRS UV-Visible and Infrared spectra of synthesized Bi⁷ Sn0.1O10.7 nanoparticles.

Fig. 4. Raman, DRS UV-Visible and Infrared spectra of synthesized Bi⁷ Sn0.1O10.7 nanoparticles.

Fig. 5. Raman, DRS UV-Visible and Infrared spectra of synthesized Bi⁷ Sn0.1O10.7 nanoparticles.

Photocatalytic activity. The photocatalytic activity of dye under visible light illumination was studied by measuring to the absorbance of the malachite green dye in presence of the (catalyst) bismuth stannate nanoparticles. The degradation was monitored, here time was increase and absorbance decreased in the malachite green concentration. Fig. 6 shows absorbance at different time intervals for the degradation of Malachite Green under visible light irradiation.

The relative concentration with time of the sample was shown in Fig. 7. Steady degradation of the dye with increase in irradiation time is observed. The complete degradation of the dye was observed with in 60 min. of visible light irradiation.

Fig. 6. Time-dependent absorption spectrum of malachite green dye solution under visible light irradiation.

Fig. 7. Degradation of dye Vs time.

Summary. Bismuth stannate nanoparticles were synthesized by hydrothermal method. The bismuth stannate nanoparticles were characterized by XRD, SEM, FT-IR, Raman and DRS-UV-Vis spectroscopy. The bismuth stannante nanomaterials have a band gap of 3.5 eV. The synthesized materials show excellent photocatalytic activity for the degradation of malachite green.

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