"Synthesis, Characterization and Photocatalytic application of $CuSnO_3$ Perovskite oxide"

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Abstract:
The present study involves synthesis of $CuSnO_3$ by using hydrothermal method. The synthesized catalyst was characterized by various investigative techniques including UV-DRS, FT-IR, XRD, SEM, EDAX, TEM and BET. The photocatalytic efficiency of $CuSnO_3$ was investigated for the degradation of Fuchsin basic dye using UV-Visible light irradiation. The recyclability of $CuSnO_3$ was also studied for the degradation and the results obtained have been discussed.

***Keywords*: Photodegradation, Fuchsin basic dye, Photocatalyst

1. Introduction:

Perovskite oxide nanocrystals have important properties in ferroelectricity, piezoelectricity, dielectricity, ferromagnetism, magneto resistance, and multiferroics. The prototype $CaTiO_3$ mineral is named for perovskite structure called perovskite, which is generally a metal oxide with the formula ABO_3, where B is a small transition metal cation and A is a larger s-, d-, or f-block cation. Perovskites with general formula ABO_3 is a kind of frequently encountered structure in inorganic chemistry. The catalytic properties of perovskite-type oxides depend mainly on the nature of the A and B ions and on their valence states. The A-site cation fits in the large cavity at the center of eight corner-sharing BO_6 octahedra, and the B-site cation resides in the interstitial site of an octahedron of oxygen anions [1]. Most of the properties of perovskite oxides are related to the network of BO_6 octahydra and the state of B-site cations [2, 3]. Perovskite type oxides have many practical applications owing to its excellent physical and chemical properties including ferroelectric random access memories, multilayer ceramic capacitors, transducers, sensors and actuators, magnetic random access memories, and the potential new types of multiple-state memories and spintronic devices controlled by electric [4-6]. It also has been shown to have high catalytic activity for the oxidation of carbon monoxide, methane, propane, Hexane and Toluene [7]. Thus, it can be used as a catalyst for combustion, automobile exhaust, and waste gas purification. Besides, it can be used as an electrode material for solid-electrode fuel cells and gas sensors [8].

All over the world is now focusing on the problem of wastewater. In recent years photocatalysis has been studied widely as a potential technology to solve the energy crisis and control environmental pollution. Photocatalytic electrolysis of water, environmental protection, solar cells, storage equipment, especially wastewater treatment and so on is the main application areas in catalysis [9]. The pollutants in waste water can be divided into organic pollutants and inorganic pollutants. Organic pollutants such as dye, pesticide, pharmaceutical waste which are very harmful to the biological safety and ecological system. Especially toxic and difficultly degradable organic pollutants (such as heavy metal pollutants, dye, pesticide) have a long half-life, and only trace can lead to biological variation [10]. Fuchsine or rosaniline hydrochloride is a dye with chemical formula $C_{20}H_{19}N_3 \cdot HCl$ [11]. It becomes magenta when dissolved in water;, it forms dark green crystals as a solid. Fuchsine is used to stain bacteria, as well as dying textiles and sometimes as a disinfectant. It is well known that production of fuchsine causes development of bladder cancers in production workers [12]. Photocatalysis, as a green catalytic technology, can almost degrade all organic pollutants without selection.

In the recent years [10] mineralization of organic water pollutants using interaction between ultraviolet radiation and semi-conductor catalysts has been widely demonstrated. The development of photocatalytic materials is important for the efficient use of solar light. Light-induced mineralization of hazardous organic pollutants with use of TiO_2 photocatalyst [13–15] has witnessed intensive studies within past two decades. There is need to search for an effective heterogeneous oxide photocatalyst for environmental cleaning purpose and test their efficacy. Organic matter from the effluents is removed by using conventional methods which lead to energy guzzling and excessive emission of CO_2; thus cause the global warming. Under such circumstances, there is need to find a new material that can work in harmony with nature and will gently restore the natural condition of water bodies by removing the pollutants by using light energy. A solution to that problem is use of the photocatalyst.

In present report, the structural and microstructural characteristics are determined for purpose of creating an inexpensive and non-toxic photocatalyst. Hence, the efforts are made to synthesize $CuSnO_3$ photocatalyst by hydrothermal synthesis method and its application for degradation of Fuchsin dye in the presence of sunlight.

2. Experimental:

2.1 Synthesis of $CuSnO_3$ photocatalyst:

Several methods are used for synthesis of photocatalytic material, which include co-precipitation [17], sol–gel method [18], hydrothermal method [19] and thin film vapour deposition method [20]. In this study, we have synthesized photocatalyst $CuSnO_3$ using hydrothermal method.

In this method, equimolar mixture of analytical grade $CuCl_2$ (1 mol) and $SnCl_4$ (1 mol) was mixed with 1N NaOH and 0.5N surfactant. This reaction mixture was stirred and then it is poured in Teflon autoclave which is kept in the oven at 20^0C for 24 hrs. After 24 hrs the product was cooled then filtered and washed with distilled water. The obtained product was dried in the oven at 120 ^{0}C for 12 hrs. Later on, the material was ground in morter and pestle and it was further calcined at 450^0C for another 3 h. Finally, polycrystalline powder of $CuSnO_3$ obtained was used for further characterization and for degradation of the dyes.

2.2 Characterization of $CuSnO_3$ photocatalyst:

The optical property of the synthesized product was studied by using UV–visible Spectrophotometer-k-950 (PerkinElmer). Copper stannate photocatalyst was scanned over wavelength range of 200-800 nm. The vibrational frequency of the synthesized catalyst was studied by FTIR-8400S (Shimadzu) in the range of 400-4000 cm^{-1}. The structural properties of the material were studied using X-ray diffractometer-DMAX-2500 (Rigaku) with Cu-Ka radiation, having k = 1.5406 A. The surface morphology and chemical compositions of synthesized catalyst were analysed using a Scanning Electron Microscope-JSM-6300 (JEOL) coupled with an energy dispersive spectrometerJED-2300LA (JEOL). TEM images were recorded onCM-200 (Philips).

3. Results and discussion:

The infrared absorption spectrum of the synthesized $CuSnO_3$ catalyst is depicted in Fig. 1. Vibrational frequency band at 354 cm^{-1} indicates the presence of Cu–O and frequency band at 613 cm^{-1} indicates the presence of Sn–O vibrations of $CuSnO_3$.

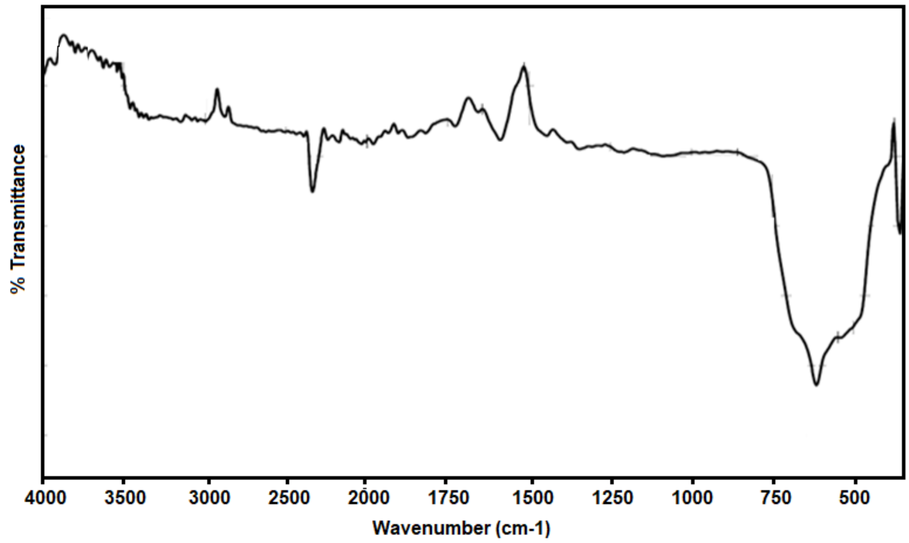

Fig. 1: IR spectra of $CuSnO_3$ Photocatalyst

Figure 2 shows XRD pattern of $CuSnO_3$ powder formed after heating. The XRD pattern recorded for pure $CuSnO_3$ (Fig. 1a) shows 2θ values along with (hkl) planes at 25.6 (100), 28.4 (110), 33.5 (200), 34.5 (200), 50.1 (101). These peaks in the XRD profile well matches with JCPDS data (Card No. 270997). The crystal structure of $CuSnO_3$ is cubic in nature.

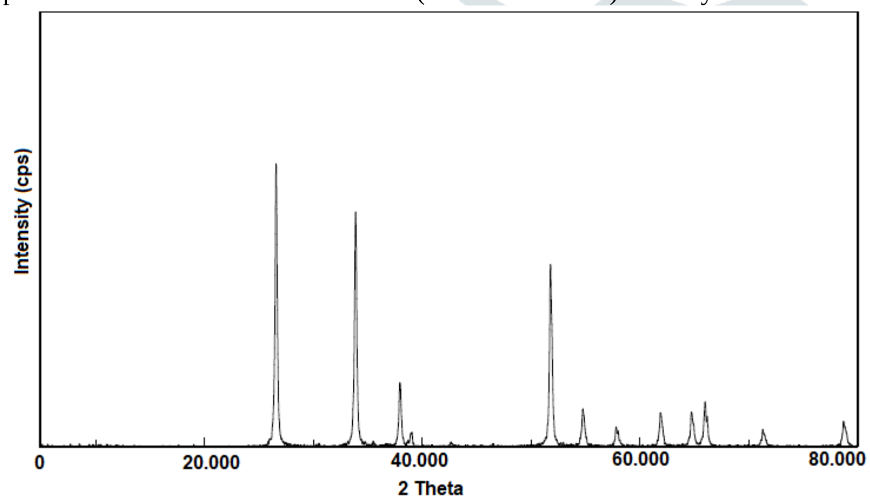

Fig. 2: XRD pattern of $CuSnO_3$ Photocatalyst.

Figure 3 represents the UV–visible diffused reflectance spectra of the synthesized $CuSnO_3$ photocatalyst. The DRS of the $CuSnO_3$ has absorption edge cut-off at 393 nm with corresponding band in the visible region. The band gap energy (E_g=hc/λ) for the compound was found to be 3.1625 eV. The broad absorption edge shoulder in the curve reveals the formation of $CuSnO_3$. The presence of uneven shape and size of $CuSnO_3$ could be one of the reasons for the broad absorption peak. The result implies that the sample may possess excellent photocatalytic activity.

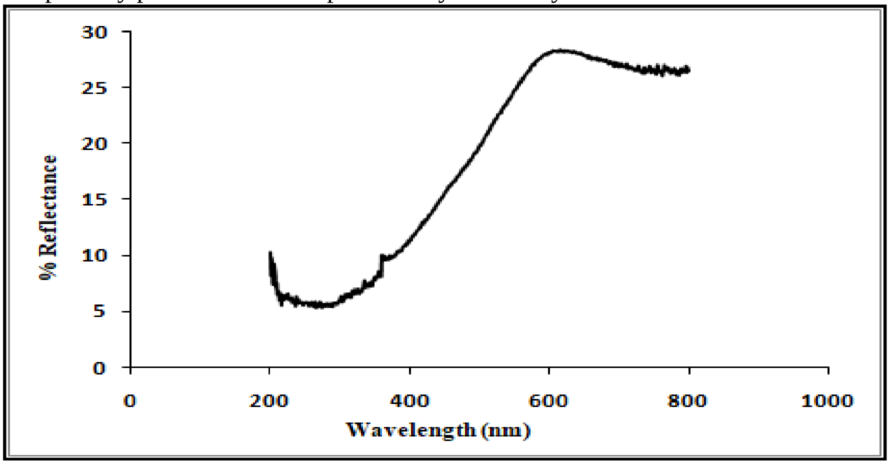

Fig. 3: UV-DRS analysis of $CuSnO_3$

The surface morphology and associated chemical composition of synthesized photocatalyst was analysed using a scanning electron microscope (SEM) coupled with EDAX and is shown in Fig. 4. The SEM image shows that the particles are agglomerating with each other. The EDAX data furnishes elemental composition in conformity with the respective molar proportions taken.

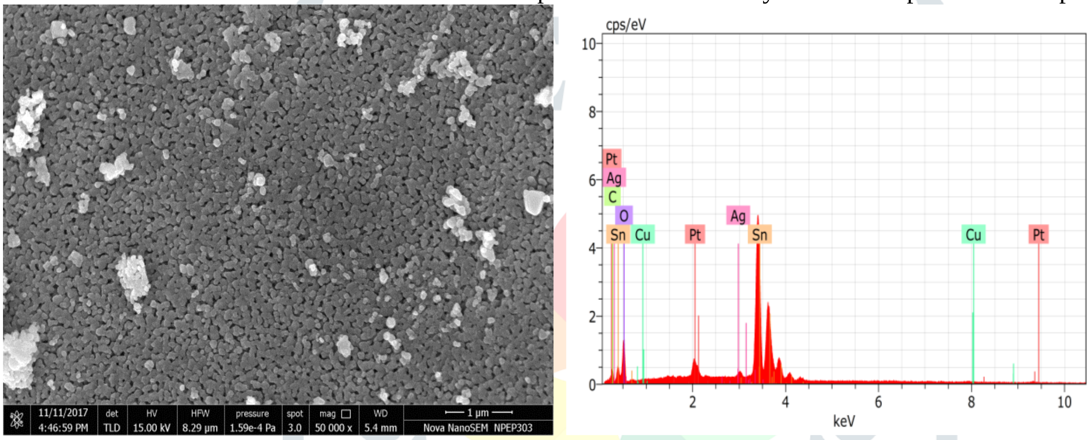

Fig. 4 SEM and EDAX analysis of $CuSnO_3$ photocatalyst.

The TEM image along with the selected area of the diffraction pattern (SAED) recorded for the sample corresponding to $CuSnO_3$ is shown in Fig. 5. The TEM reveals that, the particles are elliptical; however, there are several hexagonal-shaped crystallites. The dark spot in the TEM micrograph can be eluded to $CuSnO_3$ as SAED pattern associated with such spots reveals occurrence of cubic $CuSnO_3$ is in total agreement with the XRD data. The average size of the $CuSnO_3$ crysstals was found to be 104.5 nm.

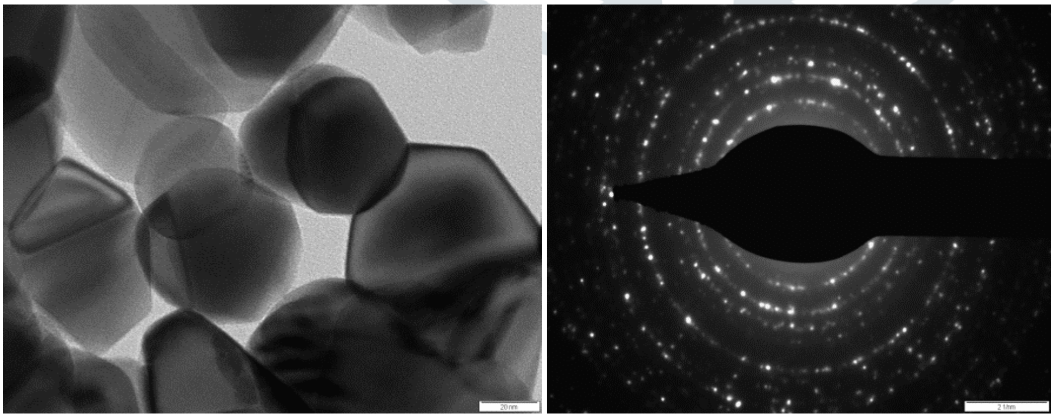

Fig. 5: TEM and SEAD image of $CuSnO_3$ photocatalyst.

4. Photocatalytic property of $CuSnO_3$:

Photocatalytic property of $CuSnO_3$, was studied by the photodegradation of 10 ppm 50 ml Fuchsin basic dye solution by measuring the absorbance after every 10 min. on double beam spectrophotometer (Systronics). The effect of amount of $CuSnO_3$ photocatalyst on degradation of dye and effect of concentration of Fuchsin basic dye was studied.

In the Figure 6 it is observed that, on increased amount of $CuSnO_3$ photocatalyst enhances the degradation of Fuchsin basic dye. The rapid degradation of dyes was observed with 0.8 gm of catalyst. This may be due to increase in amount of the photocatalyst increases ejection of number of photons and electrons in the conduction band and in the valence band, respectively. In the fig.7 it is observed that the concentration of dye increases rate of degradation of dye decreases.

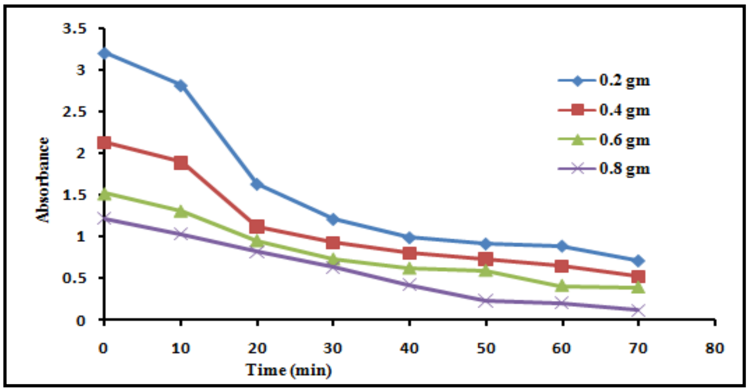

Fig. 6: Effect of amount of catalyst on degradation of dye.

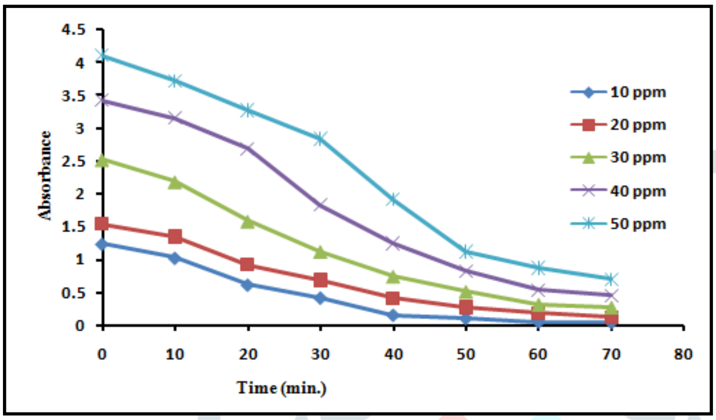

Fig. 7: Effect of concentration of dye solution on degradation using $CuSnO_3$ photocatalyst.

The chromophoric absorption peaks at 570, 590, 560, 580 and 585 nm of the solution before exposed to the UV-Visible light and photocatalyst eventually disappeared, and new peaks at 387, 317, 346, 353 and 330 nm appeared due to the mineralization after exposure to the UV-Visible light and photocatalyst. When aqueous suspension of the photocatalyst $CuSnO_3$ was irradiated with light energy greater than the band gap energy of the semiconductor oxide, conduction band electrons (e-) and valance band holes (h) are formed. The photo generated electrons react with absorbed molecular O_2 reducing it to superoxide radical anion $O_2^{-\cdot}$ and photo generated holes can oxidize organic molecules directly or the OH and the H_2O molecule adsorbed at catalyst surface to OH radical. These will act as strong oxidizing agent and can easily attack on organic molecule or those located close to the surface of the catalyst, thus leading to complete mineralization.

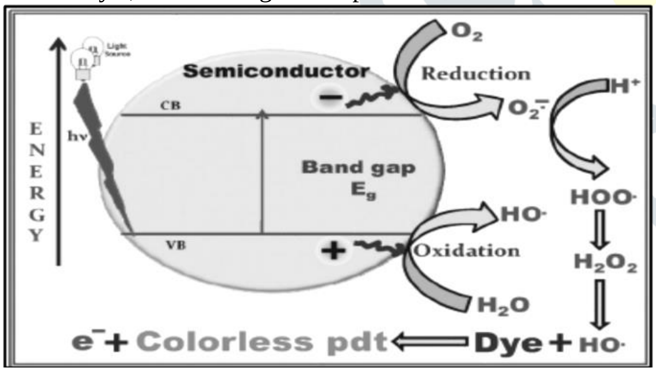

Fig. 8 General pathway of dye degradation.

5. Conclusions:

The photocatalyst $CuSnO_3$ was synthesized by using hydrothermal method. Synthesis of $CuSnO_3$ and degradation of Fuchsin basic dye were carried out without affecting aquatic life. The band gap energy of the photocatalyst was 3.1625 eV with average particle size 104.5 nm. The TEM micrograph and SAED pattern associated with spots reveals occurrence of cubic $CuSnO_3$ in total agreement with the XRD data. $CuSnO_3$ photocatalyst was effectively used for degradation of Fuchsin basic dye.

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