

Synthesis, structural and electrical conduction of some dual doped semiconductor oxides nanoparticles for photocatalytic degradation of Victoria blue-B and Brilliant yellow under solar light irradiation

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Received: 3 March 2021

Accepted: 1 January 2021

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part of Springer Nature 2021

ABSTRACT

In this study, the nanoparticles of undoped and dual (co-doped) (co-poly) semiconductor oxides such as Bi₂O₃, Bi₂(Srn_{0.50}Cu_{0.50})₂O₇, Cu₂O, Co₃O₄-Mn₂O₃, Dy₂O₃, V₂O₅, V₂O₅/Ni_{0.50}Gd_{0.50}O₃, Cu₂O, Cu₂O-Mn₂O₃, Yb₂O₃, CeO₂, and Ce_{0.50}Ni_{0.50}Zn_{0.50}O₂ were synthesized by tartarate and hydroxide coprecipitation method. The composition, structure, morphology, surface and optical properties of undoped and dual doped semiconductor oxides have been investigated by X-ray fluorescence spectroscopy (XRF), Energy dispersive X-ray spectroscopy (EDS), X-ray powder diffraction (XRD), Scanning electron micrographs (SEM), X-ray photoelectron spectroscopy (XPS), BET surface area analyzer and UV-Vis Diffuse reflectance absorption spectra (UV-vis DRS). The XRD and SEM studies show a mono-dispersion of undoped and dual (co-doped) doped semiconductor oxides in the average grain size range of 26–65 nm with a monoclinic structure for Bi₂O₃ and its doped oxide, cubic structure for Cu₂O, Cu₂O, Co₃O₄ and their respective doped oxides and orthorhombic structure for V₂O₅ and its doped oxide. Rietveld refinements of XRD pattern and XPS results confirmed that the dual dopants exist in +2 or +3 states and successfully incorporated into the semiconductor oxide matrix. BET surface areas for these oxides were found in the range of 25.3–65.4 m² g⁻¹. The band gap energy (E_g) of undoped and doped semiconductor had a direct transition to indirect between 2.10 and 3.12 eV as estimated from the optical absorption data (UV-vis DRS) and found absorption band edge (λ_g) in the visible-light range. The d.c. electrical conductivity and thermoelectric power measurements for all compounds showed n-type semiconductor except undoped and doped Cu₂O and Co₃O₄ compounds showed p-type semiconductor. The photocatalytic activity of

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<https://doi.org/10.1007/s11854-021-05272-6>

Published online: 08 February 2021

undoped and dual doped semiconductor oxides in the Victoria blue-B (VB) and Brilliant yellow (BY) solutions were studied in sunlight irradiation. A set of optimized conditions such as the amount of these oxides, initial dye concentration, pH, contact time and dopants on the photodegradation of these dyes were investigated in detail. The dual doped semiconductor oxides showed a noteworthy enhancement in the degradation of VB and BY dyes under exposure to sunlight. The enhanced photocatalytic activity can be attributed to the incorporation of multivalent dopants in semiconductor oxide matrix promoted the separation of photo-generated charges, inhibited the recombination of photo-generated carriers, and thus prolonged the charges lifetime to participate in the photocatalytic reaction. The kinetic measurements indicate the dominance of pseudo-first order rate constant for Victoria blue-B (VB) were higher than that of Brilliant yellow (BY) in all cases, indicating that the photocatalytic degradation of VB was easier and more rapid than BY dye during the adsorption and also ascribed to different molecular structure to these dyes. A tentative reaction mechanism has also been proposed for this photocatalytic reaction.

1 Introduction

Nano sized inorganic semiconductor oxides has attracted the attention of materials researchers due to its better mechanical, electrical, optical, catalytic and thermal properties, which make them technologically useful [1, 2]. The relation between the structure and properties of semiconductor oxides and their applications are of great importance [3]. Among various semiconductor oxides BaO_x , CeO_x , Cu_2O , V_2O_5 , Cu_2O have received significant attention because of its wide application in sunscreen [4], solid oxide fuel cell [5], gas sensors [6], solar cell [7], electronic ceramics [8] and catalysis [9]. Based on unique chemical and physical functionalities, of these semiconductor oxides have attracted attention, because of their interesting optical and electrical properties, visible light sensitivity and chemical stability [10, 11]. These properties depend on the synthetic method. Selection of synthetic route is crucial to control the composition, structure and morphology of chosen oxide. The various approaches were explored to synthesize of these oxides, including spray pyrolysis, sol gel method, electrospinning synthesis, sonochemical, microemulsion etc. Among, all these methods the coprecipitation method could be considered one of method that is easy to process, energy saving, environmentally friendly and cost effective as compared to other methods [12, 13].

In recent decades, metal oxides photocatalysts play an important role in the environmental field because

they may be able to degrade organic pollutants or split water [14]. The efficient use of sunlight (solar) energy for photocatalytic reactions is one of the great challenges in science and requires new technology. The photocatalytic materials, thus far applied exhibit quite low activity in visible light, which reduces the possibility for effective use of sunlight illumination in practical applications. Other major problems of photocatalytic materials are their low stability in aqueous solution, a low electron-hole pair concentration, the delayed transport properties or their photo-generated charge carriers and a decrease of activity due to recombination of electron-hole pairs during reactions. These characteristics can be improved by controlling stoichiometry and thus creating cation or anion vacancies [15]. Among the different materials, investigated for use as photocatalysts under sunlight, semiconductor oxides are regarded as promising materials due to their high photocatalytic efficiencies, low toxicity, narrow direct band gap, and high chemical stability [16]. In this way, recent papers report a new series of semiconductor oxide photocatalyst were developed as Bi_2O_3 [17], CeO_2 [18], Cu_2O [19], V_2O_5 [20], and Cu_2O [21]. These oxides are excellent candidates for degrading organic pollutants under excitation of sunlight. In addition to this, researchers have found that the doping in these oxides is an effective way to inhibit the recombination of photo-generated carriers in semiconductor oxides [22]. Accordingly, some transition metals and rare earth dopants have been investigated for BaO_x , CeO_2 , Cu_2O , V_2O_5 and Cu_2O oxides, which can improve its

photocatalysis performance started to appear in the literature [27–38]. These doping has greater potential in permitting significant optical absorptions in the visible region, through the combine effect of narrowed band gap and introduction of intermediate bands within the forbidden gap [38] and also increasing the surface defects in these semiconductor oxides [40, 41].

Recently, the simultaneous doping of two kinds of atoms into TiO_2 has attracted attention because it results in higher photocatalytic activity than single-element doping. Huang et al. found that nitrogen–fluorine co-doped TiO_2 showed high visible light activity and found about 1.5 times higher than that of single-doped TiO_2 [42]. This is due to the generation of additional band in the forbidden gap and the synergistic effect permitting to tune the electronic structure and also enhance the visible light photocatalytic activity [43]. Similarly, more recently, the structural, optical and electronic properties of (Co,Ni) reduced CeO_2 nanoparticles have been reported in literature, but no photodegradation of dye studied and claimed oxygen vacancies related defects are increasing with codoping [44, 45]. So far, very less work has been reported in literature using co-doped semiconductor oxides.

Inspired by above mentioned investigations, we report the dual doped (co-doped) divalent and trivalent metal ions of transition and/or rare earth elements on Bi_2O_3 , CeO_2 , Co_3O_4 , V_2O_5 , and Cu_2O photocatalyst were obtained via a simple tartarate or hydroxide coprecipitation method. The intrinsic characteristics were studied in terms of the results from XRD, SEM, XPS, BET techniques, electrical conductivity and UV–visible spectroscopy. In addition, the photocatalytic activity of the as synthesized undoped and dual doped of these oxides was deeply investigated by observations and photodegradation of Victoria blue-B (VB) and Brilliant yellow (BY) dye solutions under sunlight irradiations.

2 Materials and methods

2.1 Synthesis of undoped and doped precursors

2.1.1 Bismuth tartarate perchlorate, $\text{Bi}(\text{C}_2\text{H}_3\text{O}_7)_2 \cdot 5\text{H}_2\text{O}$

Bismuth tartarate was prepared by the coprecipitation method by taking $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.410 g) in

double distilled water (100 ml). The solution was placed in three necked flask under a stream of dry nitrogen atmosphere to prevent the air oxidation of ions. The pH of the medium was adjusted to a low enough value (pH < 3), so that hydroxide precipitate does not form. The solution was stirred vigorously with a magnetic stirrer at 60 °C. To this di ammonium tartarate (8.887 g dissolved in 50 ml distilled water) solution was added slowly with stirring till a permanent precipitate occurred. Acetone was added in equal amounts. Here the addition of acetone not only ensured high yield, but also influenced the homogeneity, stoichiometry, and transparency of the particles of bismuth tartarate. The resultant precipitate of $\text{Bi}(\text{C}_2\text{H}_3\text{O}_7)_2 \cdot 5\text{H}_2\text{O}$ was ivory in colour. The solution was filtered after stirring it for 30 min. The precipitate was washed several times with cold distilled water and then with acetone to speed up the drying. It was air dried at the ambient temperature.

Bi with Sn and Cu doped bismuth tartarate precursors was synthesized following the same procedure by taking samarium nitrate (0.487 g) and copper nitrate (0.265 g) as dopant. The schematic flow chart for the synthesis of doped bismuth tartarate precursor and subsequent conversion to dual doped (co-doped) bismuth oxide is shown in Fig. 1a.

Other dicarboxylate coprecipitates were prepared by following the procedure given above. The additional relevant details are summarized below.

2.1.2 Cerium tartarate perchlorate, $\text{Ce}(\text{C}_2\text{H}_3\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$

This precursor was prepared by taking ceric nitrate, $\text{Ce}(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$ (12.634 g) in double distilled water (50 ml). To this di ammonium tartarate solution (12.036 g dissolved in minimum distilled water) was added slowly with stirring, till a permanent precipitate was occurred. The white precipitate was filtered and washed with distilled water and air dried at ambient temperature.

Similar procedure was used for the synthesis of 10 wt % Ni and Zn doped cerium tartarate by taking the stoichiometric amount of nickel nitrate (0.444 g) and zinc nitrate (0.454 g) as dopant.

2.1.3 Cobalt tartarate perchlorate, $\text{Co}(\text{C}_2\text{H}_3\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$

This precursor was prepared by taking $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (5.928 g) in double distilled water (50 ml). To this di