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Original research article

Synthesis, characterization of Bi/ZnO and its photoactivity towards TB, AR 27 & RR 120 degradation under UV-A light

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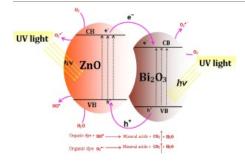
Highlights

- The catalyst was prepared by simple solvothermal method.
- · The catalyst is found to be stable and reusable.
- Complete mineralization was achieved.
- Treatment of dye effluent using Bi/ZnO will be more economical and eco-friendly.

Abstract

Bare and hexagonal wurtzite Bismuth loaded ZnO (Bi/ZnO) nanostructures have been prepared successfully by a simple solvothermal method. The structure and composition of the samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), energy dispersive spectrum (EDS), diffuse reflectance spectra (DRS), photoluminescence spectra (PL), cyclic voltammograms (CV) and BET surface area measurements. In the present work, the photocatalytic degradation of Trypan blue (TB), Acid Red 27 (AR 27) and Reactive Red 120 (RR 120) dyes with prepared heterogeneous photocatalyst under the UV-A light. Bi/ZnO was found to be more proficient in the degradation of TB, AR 27 and RR 120 dyes than bare, commercial ZnO and Bi₂O₃. The mineralization of these three dyes have been confirmed by Chemical Oxygen Demand (COD) measurements. A possible mechanism was proposed for Bi/ZnO under UV light. This catalyst can be reused and it provides more stability.

Graphical abstract



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Introduction

The azo compound class accounts for 60-70% of all dyes. As you valor expects, they all contain an azo group, -N = N-, which links two SP² localized carbon atoms. Often, carbon atoms are the part of aromatic systems, but this is not always the case. Most dyes contain only one azo group, but some contain two, three or more. The usage of azo dyes in dyeing textile fibers, particularly cotton but also silk, wool, viscose and synthetic fibers. They are considered to be easy to use, and relatively very cheap and also to provide the more intense colors to the dye. There are roughly more than 2000 azo dyes available in the market.

Most of the azo dyes are water soluble and are therefore it very easy for the body to adsorb, as well as skin contact through inhalation and swallowing of dust particles. Azo dyes may also be toxic to human as well as aquatic organisms and also produce long-term adverse effects in the living things [[1], [2], [3], [4]]. In addition to that, the textile industry also produces waste water or effluent with high coloring nature, it creates both environmental and aesthetic problems. Due to the slow degradation, these effluents are considered as non-biodegradable pollutants or environmentally hazardous [[5], [6], [7]]. For that reason, now a day's researchers are focused to develop the modern technology used to solve the issues. Catalysts plays a vital role for the global energy cries problem and very severe environmental pollutions. Especially, heterogeneous photocatalyst like TiO₂, ZnO, SnO₂, WO₃, Bi₂O₃, ZnS, CdS, Ag₂S, AgBr etc., plays a immense responsibility in the field of degradation process [[8], [9], [10], [11], [12], [13], [14]].

In most of the cases, under UV light TiO₂ or ZnO have been employed for the photo degradation process of toxic dyes [[15], [16], [17], [18], [19], [20]]. But when compared TiO₂, ZnO is more auspicious for detoxification studies under UV light irradiation, due to its stability, reusability and very simple preparation technique. Furthermore, conquest of the recombination of photogenerated electron–hole pair in the semiconductors the photocatalytic property has been reduced. Doping of metals on the semiconductor oxide is huge useful way to improve the charge separation property [21]. Numerous dopants such as transition metals or inner transition metals could increase the catalytic activity of ZnO [[22], [23], [24], [25]]. Especially, Bismuth is a pentavalent post-transition metal and one of the pnictogens [26]. It is a brittle metal with a white, silver-pink hue, often occurring in its native form with an iridescent oxide tarnish showing many colors from yellow to blue. It is also having super diamagnetism with a different physical phenomenon like lowest thermal conductivity, highest hall coefficient and high electrical resistance. Moreover, Bi³⁺ metal is deposited in sufficiently thin layers on a substrate, bismuth is a semiconductor (Bi₂O₃), rather than a poor metal. So, interested in participating in our study, a simple precipitation-decomposition process aided by solvothermal method is developed for the synthesis of Bi/ZnO superstructures. The prepared material shows an advanced activity and thus displays physically powerful heterogeneous photocatalytic effectiveness in the photodegradation of Trypan Blue, Acid Red 27 and Reactive Red 120 dyes under UV-A light.

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Section snippets

Preparation of catalyst

Bi/ZnO NPs was prepared by a simple solvothermal method. Aqueous solutions appropriate amount of 0.4 M zinc nitrate hexahydrate and of 0.6 M oxalic acid were heated to 90 °C discretely. Zinc oxalate suspension was precipitated, due to the addition of oxalic acid to zinc nitrate solution. A solution of Bi $(NO_3)_3$.5H₂O in 5 mL of water was added to this precipitated mixture then heated to 60-70 °C and stirred for 5 h. It was cooled to room temperature. The mixture was washed with several time with

Results and discussion

TB with different wt% of Bi on ZnO was carried out using photocatalytic experiments. *Pseudo*-first order rate constants were determined for 0.5, 1.0, 1.5 & 2.0 wt% of 'Bi' loading were 0.0860, 0.1340, 0.0897, 0.0789 and 0.0754 min⁻¹ respectively. 1.0 wt% of Bi/ZnO was found to be the most efficient. Hence, 1.0 wt% of 'Bi' was taken as optimum concentration of Bi/ZnO and this catalyst was characterized by numerous studied.

Fig. 1 show the XRD patterns of the bare ZnO, Bi₂O₃ and Bi/ZnO powders. For

Photo catalytic degradation of TB

A control experiment was carried out on the irradiation of TB under only UV light, in the presence of Bi loaded ZnO (Bi/ZnO) with and without light irradiation, as shown in Fig. 8. No degradation was observed in the absence of UV light (curve c). The results also show that there was negligible degradation (0.2%) when the reaction was allowed to occur in the presence of UV light without any catalyst. About less than 1% decrease in dye concentration was occurred due to adsorption for the

Chemical oxygen demand (COD) measurements

To confirm the mineralization of TB, the degradation was also analyzed by COD values. After one-hour irradiation with bare ZnO (79.3%), Bi_2O_3 (67.5%) and Bi/ZnO (99.1%) of COD reduction is obtained. This indicates that Bi loaded ZnO was achieved almost complete mineralization of dye.

Mechanism of the degradation

A mechanistic scheme of the charge separation and photo catalytic reaction for Bi/ZnO photo catalyst is shown in Scheme 2. When ZnO semiconductor irradiated by UV—A light, a valence band electron (VB) is promoted to conductance band (CB) leaving a hole in valence band. Catalytic activity is increased due to the decrease of electron hole recombination. The energy levels of Bi₂O₃–ZnO coupled system are suitable for vectorial electron transfer. (CB potential of Bi₂O₃ (+O.11 eV) is more positive

Conclusions

Bi/ZnO catalyst was prepared by simple solvothermal process. It was characterized by XRD, FE-SEM, EDS, DRS, PL, CV and BET measurements. XRD spectra of Bi/ZnO it is inferred that the diffraction pattern 2θ values and the corresponding (hkl) values are found to be same for single phase ZnO. The crystalline size of bare ZnO, Bi_2O_3 and Bi/ZnO was determined using Debye-Scherrer equation. The crystalline size of the Bi/ZnO NPs was 6.2 nm, lower than that of the bare ZnO (17.2 nm) & Bi_2O_3 (12.3 nm).

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...Therefore, various scientific efforts are currently under development in advocating the energy-efficiency of UV/ZnO system, in concurrent to visible light or solar light system. One of the common strategies is to introduce impurity dopant (Jung et al., 2018; Ahmadi et al., 2018; Azarpira et al., 2019; Sasikala and Subash, 2019; Meenakshi and Sivasamy, 2018) that reduces the recombination rate of charges-carriers, while others focus on photocatalytic system improvements (Samy et al., 2020; Sarkhosh et al., 2019; Zhang et al., 2017) and employment of energy-efficient activator, such as UV-LED (Vaiano et al., 2018a, 2018b; Dai et al., 2014; Sampaio et al., 2017) for the betterment of photocatalytic performances. Indeed, these strategies are well-accepted as the important keys to unlock the industrialization of UV/ZnO system, particularly for organic wastewater treatment....

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