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Sunlight assisted photocatalytic degradation of different organic pollutants and simultaneous degradation of cationic and anionic dyes using titanium and zinc based nanocomposites

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Highlights

- ZnO-TiO_2 nanocomposites have been prepared by hydrothermal method.
- Composites are nano-crystalline having TiO_2, ZnO, Zn_2TiO_4 and other zinc titanates.
- The average crystallite size of the prepared nanocomposites was between 8 and 36 nm.
- Photocatalytic degradation of organic pollutants has been studied by composites.

- ZnTi-2:1 (Zn_2TiO_4/ZnO) has shown excellent activity as compare to other catalysts.

Abstract

ZnO-TiO_2 nanocomposites have been successfully synthesized by using simple hydrothermal method with various ZnO-TiO_2 concentrations (such as 2:1, 1:1 and 1:2 ZnO-TiO_2, pure ZnO and TiO_2). The XRD, FT-IR, HR-TEM, FE-SEM with EDAX, XPS and UV–Visible spectroscopy were utilized for characterization of the as-prepared products. XRD revealed that samples are in nanocrystalline nature with formation of anatase TiO_2, hexagonal ZnO, cubic Zn_2TiO_4 and other zinc titanates. The average crystallite size of the samples was between 8 and 36nm. The photocatalytic activity has been demonstrated for the degradation of methylene blue (MB), tetracycline (TC) and mixture of dyes (includes methylene blue, rhodamine B and methyl orange) under sun light irradiation at room temperature. The degradation rate of methylene blue has been significantly enhanced with increase in percentage of ZnO. Nanocomposites with 2:1 concentration of Zn and Ti, has been more efficient than that of other composites. Also, effect of different parameters such as pH of dye solution, concentration of dye and amount of catalyst etc. has been evaluated.

Introduction

Currently whole world suffering from environment issue such as lack of substantial and clean natural energy, pollution, contamination of the environment. The fast growing industrializations have increased the generation of highly toxic and carcinogenic wastewater. The wastewater includes high concentration of various organic dyes, surfactants, heavy metals and other harmful compounds which also hazardous to the quality of soil and introduce ill-effect on aquatic ecosystems as well as human beings [1]. From them dyes and pigments are substances with high application potential in the various industries and extensively used in textile, food, cosmetic, precious stones, leather, paper, plastics, processing, printing, rubber, pharmaceutical, tannery primarily to color the final products [2]. During the process of colouring, 10–50% dyes are losses and discharged in to the wastewater that generate coloured effluents. For example, it is estimated that there are more than 100,000 synthetic dyes, with an annual manufacture of more than 700,000 tons world-wide, producing a significant amount of wastewater [3]. In the textile effluent the concentration of dyes are differs from 10 mg/L to 250 mg/, the highest concentration 800 mg/L of reactive dye referred by Yaseen and Scholz [4], [5]. Furthermore, tetracycline (TC) is frequently used as antibiotics, which on discharge to water system develops considerable adverse effects on human health and ecological systems. Due to the poor decomposition in animals and human bodies, the majority of TC is discharged into the wastewater [6]. Furthermore, antibiotic existence in the environment can affect various species of bacteria, and increase their resistance [7], thus it needs appropriate approaches for its removal.

Numerous technologies have been widely investigated to remove the concentration of dye and tetracycline from wastewater. In which photocatalytic technology is an emerging and severally demonstrated with prominent superiority for the decomposition of organic dyes, pollutants and pharmaceutically emerging contaminants from different industries, health care sector as well as agriculture field. Semiconductor composite photocatalysts have been extensively exploited in recent years owing to their promising properties due to individual components and newly introduced properties due to formation of composite. Several composites has been used for addressing the pressing task to curb the current rapid deterioration of the living environment [8]. Primarily, in photocatalysis decomposition of organic and inorganic compounds has been initiated through the generation of electron-hole pairs. Photocatalyst illuminated with light of energy higher than its band gap, which results in excitation of electrons from the valence band (VB) to the conduction band (CB), leaving holes in the VB. These photo excited electrons and the generated holes could help to deoxidize or oxidize adsorbates on the catalyst surface.

Among various semiconductor photocatalysts, titanium oxide (TiO_2), especially with the anatase phase, is one of the most attractive and exploited catalyst due to its several properties, which includes chemical stability, inexpensiveness, high crystallinity, strong oxidation and reduction properties, non-toxicity, and light-scattering properties [9], [10]. However, TiO_2 has a wide band gap energy (3–3.2 eV). It limits the photocatalytic applications of TiO_2 under sunlight irradiation as it needs ultraviolet light for activation and generally sunlight having less than 5% UV light [11]. From last few decades, improving TiO_2 photocatalytic efficiency has become a hot topic. One of commonly used approach is doping of transition metals/non-metals into TiO_2, forming doped photocatalyst, which would modify both physical and optical properties of TiO_2 [10], [12], [13]. Another approach is to couple the TiO_2 with other oxides in order to achieve higher photocatalytic efficiency. These metal oxides includes WO_3 [14], ZrO_2 [15], ZnO [16], [17], [18], SiO_2 [19], [20], Fe_2O_3 [21], SnO_2 [22] and MoO_3 [23]. Like TiO_2, zinc oxide (ZnO) is another promising n-type semiconductor photocatyst, which has received a great attention. ZnO having wide band gap of 3.37 eV and used efficiently for organic pollutants photodegradation[24], [25], [26], [27], [28], [29], [30], [31]. Further, it is attracting researcher due to its nontoxicity, high catalytic efficiency and low cost [32], [33], [34], [35]. But, due to large band gap energy ZnO photocatalyst is also applicable under UV irradiation [36]. Also, ZnO suffers from intrinsic drawback of photocorrosion, which resembles its photoactivity and photostability [37]. Further, several research activities have been applied to enhance the photocatalytic properties by introducing nanostructures or morphologies of TiO_2 as well as ZnO [38], [39], [40], including polymer backing [41], surface doping with nonmetallic/metallic elements or semiconductor oxides [10], [12], [13], [42], [43], [44], [45], and surface deposition/composites of metal nanoparticles [46], [47], [48]. TiO_2 catalyst can be coupled with ZnO in the form of composite to enhance photocatalytic efficiency by reducing the charge carrier recombination rate and improving its visible-light photocatalytic activity [49], [50], [51].

Furthermore, coupling of nanosized TiO_2 and ZnO has been well-established and remarkably improve the separation efficiency of photo excited charge carriers due to the formation of heterojunction structure between these two, thus improving quantum efficiency as well as photostability of the catalyst [52], [53]. Though the binding energies of ZnO and TiO_2 are comparable to each other, the potentials of the CB and the VB of ZnO are bit more negative than those of TiO_2 [54], [55]. Accordingly, lower band gap energy may be achieved when TiO_2 and ZnO were combined in an appropriate way [56], [57].

ZnO-TiO_2 nanostructured composites were very active materials due to its unique properties. These nanocomposites were multifunctional semiconductor materials with a direct wide-band gap and large excitation binding energy. Nanostructured semiconductor ZnO-TiO_2 nanocomposite were synthesized using various techniques like sol–gel, hydrothermal, solution combustion, co-precipitation, ultrasonic precipitation, ball milling technique, and thermal decomposition [58], [59], [60], [61], [62].

In this present study, we have developed a facile and reproducible strategy for preparing ZnO-TiO_2 and ZnO/Zn_2TiO_4 nanocomposites by hydrothermal method. The prepared nanocomposites were characterized by X-ray diffraction spectroscopy (XRD), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX), high resolution transmission electron microscopy (HRTEM), and UV–Vis diffuse reflectance spectroscopy (UV-DRS), etc. The photocatalytic activity of the as-prepared photocatalyst was measured by the degradation of methylene blue (MB), mixture of dyes and tetracycline antibiotic. The nanocomposites displayed significantly enhanced photocatalytic activity than pure TiO_2 under direct sun light irradiation.

Section snippets

Preparation of mixture A:

5.60 g of zinc acetate dihydrate was dissolved in 50 ml water under vigorous stirring at 60 °C. 10 ml 0.5 M sodium hydroxide solution was added dropwise into zinc acetate aqueous solution until a transparent solution was obtained (at pH = 9). Resultant solution was stirred at 60 °C for 30 min.…

Preparation of mixture B:

The 7.593 ml of acetic acid was added in to 75 ml of ethanol under continuous stirring for 30 min. Then 7.593 ml of titanium tetra-isopropoxide was also added to acetic acid solution and stirred for…

X-ray diffraction study:

The X-ray diffraction patterns of ZnO, TiO_2 and ZnTi-1:1, ZnTi-2:1, ZnTi-2:1 are shown in Fig. 1. Bare ZnO has shown the characteristic peaks at 31.81°, 34.5°, 36.32°, 47.65°, 56.69°, 62.93°, 68.00° and 69.23°, which are correspond to (100), (002), (101), (102), (110), (103), (112) and (201) crystal planes respectively, associated with wurtzite type of ZnO, which indicate that ZnO possesses a hexagonal crystal structure. Whereas, for pure TiO_2 diffraction peaks are located at 2θ = 25.25°,…

Conclusion

In this study, have successfully prepared ZnO/TiO_2 and $TiZn_2O_4$/ZnO nano-composites by using hydrothermal methods. XRD, SEM and TEM shown that the prepared catalysts are nanocrystalline in nature. Further, SEM shows the rod and spherical particles in the catalysts. These as-prepared nanocomposites has shown good efficacy for photocatalytic degradation of methylene blue dye, mixture of dyes and emerging contaminant tetracycline. ZnTi-2:1 catalyst has been recycled for three times without loss in…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

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