Synthesis of bi-metallic oxides nanotubes for fast removal of dye using adsorption and sonocatalysis process

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ABSTRACT

In this study, ultrasound-assisted synthesis of bi-metallic oxides nanotubes (ZnO–TiO$_2$ NTs) using sol–gel method followed by hydrothermal method is reported. Essentially, an attempt was made to investigate the simultaneous adsorption and sonocatalysis process for fast removal of dye using ZnO–TiO$_2$ NTs. The results of characterization revealed that ZnO–TiO$_2$ NTs were hollow nanotubular structure in shape with tube diameter of ∼10 nm and open ended. It has large specific surface area of 336.9 m^2/g as compared to ZnO (30.5 m^2/g) and TiO$_2$ (12.3 m^2/g). The band-gap energy of NTs is 2.95 eV which is much lower than the pure ZnO (3.18 eV) and TiO$_2$ nanoparticles (3.15 eV). Activity of ZnO–TiO$_2$ NTs was assessed using decolorization process as model reaction system involving adsorption and sonocatalysis processes. The results were also compared with their counterparts, *viz.* ZnO and TiO$_2$. Experimental results revealed that large specific surface area and surface charges on ZnO–TiO$_2$ NTs promote the adsorption efficiency, while the high pore volume helps dye molecules to diffuse rapidly during the sonocatalysis process. Approximately, 97% of decolorization was achieved within 10 min of treatment with sonocatalysis process. These experimental results presented in this paper could form a useful tool for further research in degradation of other bio-recalcitrant pollutants using ZnO–TiO$_2$ NTs.

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Introduction

In last decades, several efforts have been committed to improve the degradation/mineralization efficiency of bio-recalcitrant pollutants from industrial wastewater, especially hydrophilic compounds. Recently, the most widely used techniques for treatment of wastewater discharge from several chemical and process industries are sonolysis, photolysis, Fenton, ozone, ferrioxalate *etc.* [1–6]. The heterogeneous sonocatalysis or sonophotocatalysis process for degradation in presence of different catalysts is becoming more popular due to enhanced degradation rate and reusability of the catalysts [7,8]. One of the low cost, non-toxic, high chemical stability and easily available catalyst for sonocatalysis reaction is TiO$_2$. Another promising and an excellent *n*-type semiconductor used in catalysis reaction is ZnO, which also exhibits degradation efficiency as good as TiO$_2$ nanoparticles [8,9]. More recently, many researchers have focused on catalyst's modification to enhance the catalytic activity by doping with transition metals (Fe-, Co-, Ni-, Ru-, Cu-, Au-, Ag-) [10–14] or 2D layered materials (such as graphene, MoS$_2$ *etc.*) [15]. Other fascinating class of the materials is the metal oxide nanotubes, which attracted the researchers due to their potential applications in a myriad of fields such as sonocatalysis, photocatalysis etc. for extended degradation of bio-recalcitrant pollutants from aqueous solution [7,16,17]. Moreover, nanotube also has intrinsic advantages over their counterparts of nanoparticles in terms of physiochemical properties and shape-dependent structure [18,19].

However, due to low penetrability of ultraviolet light in liquid medium, high catalyst concentration and screening effect by the catalyst could bound the electron excitation in photocatalysis process and limits to a certain level of degradation/mineralization [16,20]. Another formidable challenge is reduced recombination rate of photo-generated electron–hole (e$^-$–h$^+$) pairs; and sometimes photo-corrosion leading to significant reduction in photo-activity and stability [17]. Thus, it is highly desirable to synthesis a promising materials with high catalytic activity and dual

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functioned materials. Sonochemical technique, a relatively new and advanced technique [8,21,22], has gained the popularity for synthesis of such nano-materials as it does not use any toxic reagents, additives as promoter or stabilizer during the reactions. Hence, the sonochemical route always increases the purity of the products [23,24]. In sonochemical synthesis of materials, several effects are responsible for formation of nano-materials. These are categorized as primary sonochemistry, which is a gas-phase chemistry occurs inside the bubble during transient collapse; secondary sonochemistry which is basically a solution-phase chemistry occurs outside the bubbles or bulk liquid medium; and physical modifications due to the micro-turbulence and shock waves derived from the collapsing bubble [21,24,25].

In this study, sonochemical synthesis of bi-metallic oxide nanotubes and their application in wastewater treatment for rapid removal of recalcitrant pollutants has been investigated. Bi-metallic nanotubes of ZnO–TiO$_2$ have been synthesized using ultrasound-assisted sol–gel method followed by hydrothermal treatment. To assess the activity of synthesized ZnO–TiO$_2$ NTs, decolorization process was chosen as model reaction system and Methylene Blue as model compound. Essentially, decolorization process was investigated using three techniques sonolysis, adsorption and simultaneous application of these techniques. The efficacy of ZnO–TiO$_2$ NTs in decolorization was also compared with pure ZnO and TiO$_2$ nanoparticles in presence and absence of ultrasound.

Experimental

Chemicals

Titanium(IV) isopropoxide (TTIP) and Methylene Blue (MB) were purchased from Alfa–Aesar and Loba Chemie India Ltd., respectively. Zinc acetate dehydrate (ZnC$_4$H$_6$O$_4$), ZnO, anatase TiO$_2$, ethanol, glacial acetic acid, ammonium solution (30%), sodium hydroxide (NaOH) and potassium hydroxide (KOH) were purchased from Merck India Ltd. The chemicals have been used as received without further pretreatment. Millipore water from millipore synthesis unit (Millipore®, USA) has been used to prepare the solutions in all experiments.

Synthesis of ZnO–TiO$_2$ nanotubes

ZnO–TiO$_2$ NTs was synthesized using ultrasound-assisted sol–gel technique followed by hydrothermal treatment. An ultrasonic processor (Sonics & Materials Inc., model: VCX500, power: 500 W) with working frequency of 20 kHz was used for synthesis of ZnO–TiO$_2$ NTs. Ultrasound irradiation was applied to the solution using 5 s ON–5 s OFF mode with 40% amplitude and this procedure has been followed throughout the synthesis. First, solution A was prepared by mixing 29 mL ethanol, 1 mL acetic acid and 2 mL TTIP. The mixture was sonicated for 10 min followed by addition of 20 mL water giving the final concentration of Ti in the solution as 0.1351 M. In another beaker, solution B was prepared by dissolving 1.4828 g of zinc acetate dihydrate in 49 mL of water and sonicated for 10 min. During the sonication, 1 mL of ammonium solution was added drop-wise in silent period making the final concentration of Zn as 0.1351 M. Then, both the solutions (A and B) were mixed giving the Zn:Ti molar ratio of 1:1 and the mixture was sonication for another 20 min. The resulted sol–gel was dried under hot air oven at 100 °C over night.

A hydrothermal method was followed to synthesis ZnO–TiO$_2$ NTs as reported by Pang et al. [16]. Briefly, in a mixture of 98 mL of 10 M NaOH and 2 mL of 10 M KOH solution, 3 g of synthesized ZnO–TiO$_2$ powder was mixed and heated at 100 °C under reflux for 48 h. The resulted powder was washed with millipore water

for several times to remove excess Na$^+$ ions. To confirm the complete removal of Na$^+$, the powder was also treated with 0.1 M HCl. This procedure was continued until the pH of washing solution reached to 3 followed by washing with millipore water and dried under hot air oven at 100 °C for 12 h. The obtained ZnO–TiO$_2$ powder was calcined at 300 °C with 10 °C/min ramping for 3 h. In order to prevent the loss of tubular morphology and specific area, a special care was taken so that calcination temperature does not go beyond 300 °C [16].

Procedure for decolorization experiments

Experiments were conducted using either mechanical stirring at 300 rpm (Tarson, model: MC-02) or an ultrasound bath (JeioTech, South Korea, model: UC-10). Ultrasound bath operates at a frequency of 40 kHz and a theoretical power of 200 W. The dimension of the ultrasound bath was: L = 300 mm, W = 240 mm, and H = 240 mm. The pressure amplitude of the bath was determined as 1.9 bar using calorimetric technique with volumetric energy dissipation to the medium of 8.71 W/L [26,27].

In order to investigate the decolorization process, three different techniques, viz. sonolysis, adsorption and sonocatalysis, have been adopted. In a typical experiment, 50 mL of MB dye solution with an initial concentration of 0.063 mM (20 mg/L) was taken and 25 mg (or 0.5 g/L) of catalyst (ZnO or TiO$_2$ or TiO$_2$–ZnO NTs) was added to the solution. Then the reaction mixture was placed under ultrasonic irradiation for 20 min. The initial pH of the reaction solution was adjusted to 7 and it was left uncontrolled throughout the experiment. The temperature of the bath, hence the reaction solution in the beaker, was controlled at 25 ± 1 °C by circulating cooling water from cooling water bath (Amkette Analytics, model: WB2000). After the treatment, the sample was collected and the solid particles were separated using centrifugation at 5000 rpm for 20 min (Remi Equipment, model: R-8C). Then the residual dye concentration in the sample was analyzed using UV–vis spectrophotometer (Perkin Elmer, model: Lambda 35). Each experiment was conducted for at least twice and the average value has been used to plot the graphs.

Results and discussion

Transmission electron microscope (TEM) analysis

The surface morphologies of ZnO, TiO$_2$ and ZnO–TiO$_2$ NTs were analyzed using Transmission Electron Microscope (JEOL, model: JEM2100, USA) and depicted in Fig. 1. It clearly shows that ZnO and TiO$_2$ nanoparticles are isotropic in shape and uniform in terms of size distribution; while ZnO–TiO$_2$ NTs was hollow nanotubular structure in shape with tube diameter approximately 10 nm and open ended. The length of the nanotubes was in the range from several hundred nanometers to micrometers.

X-ray diffraction (XRD) analysis

The structural characteristics of the powders were analyzed using X-ray powder diffractometer (Bruker, model: D8 Advance) with monochromatic Cu-K_α (λ = 1.5406 Å) radiation. Fig. 2 shows the XRD patterns of the samples. A strong peak observed at 2θ = 25.4 corresponds to the predominant (1 0 1) anatase phase with other crystal planes of TiO$_2$ at (0 0 4), (2 0 0), (1 0 5), (2 1 1), (2 0 4), (3 1 1) and (1 1 2) [8,17,28,29]. The peaks observed at (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) are the characteristic peaks of ZnO. Peaks, (0 0 2) and (1 0 1), at 2θ values of 34.4 and 36.23 indicate hexagonal wurtzite structure; while the peaks at (1 0 2) and (1 0 3) indicate the wurtzite crystal structure of ZnO [30]. The XRD patterns show that ZnO–TiO$_2$ NTs were