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Synthesis, characterization and visible light photocatalytic activity of carbon and iron modified ZnO

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Abstract In the present work visible light active C and Fe modified ZnO photocatalysts were prepared using microemulsion method. The obtained samples were characterized by TG-DTA, XRD, FT-IR, XPS, SEM, EDX, TEM, PL and UV–visible spectroscopy. XRD study reveals that C and Fe modified ZnO have hexagonal wurtzite structure. As the concentration of Fe changes, morphology of ZnO also changes from rod like shape to spherical shape. It was found that C, Fe co-doping improves the photoabsorption capacity of ZnO in visible region (red shift is observed). XPS study reveals that C and Fe are successfully doped into ZnO lattice with Iron in Fe (III) state. PL quenching for C, Fe co-doped ZnO photocatalysts indicates lower recombination rate of excited electrons/holes. As compared to undoped and C doped ZnO, and Fe doped ZnO, the C, Fe co-doped ZnO photocatalysts exhibited much higher photocatalytic activity for 2,4,6-trichlorophenol (TCP) degradation under visible light irradiation. The optimal ratio of Fe is found to be 2.07 wt%. Stability of photocatalyst was investigated up to fourth cycle and is found to be very stable.

1. Introduction

Rapid industrial development in recent years leads to release large number of toxic pollutants into the environment which are hazardous to human health. Among these pollutants, phenolic compounds are very toxic, hazardous and common in industrial waste water originating from coal conversion and petroleum refining industries. Chlorophenols are used as herbicides, pesticides and wood preservatives and at natural conditions they may transform to more hazardous compounds (Anisuzzaman et al., 2015; Skurlatov et al., 1997; Park et al., 2002). The presence of 2,4,6-trichlorophenol (TCP) leads to serious impact on water quality. It shows adverse effects on the human nervous system and cause many health disorders (Bashiri and Rafiee; Vinita et al., 2010). Therefore, it is necessary to find innovative and cost-effective methods for the safe and complete destruction of these chlorinated compounds. Several traditional techniques like activated carbon

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adsorption, biological treatment, chemical oxidation, etc are used to remove these compounds from waste water. But these techniques are having certain drawbacks. For example, activated carbon adsorption technique based on phase transfer and does not decompose the pollutant. In biological treatment technique microbes are used to degrade chlorophenols. However, this technique is inefficient as chlorinated phenols are resistant to biodegradation, within acceptable time period and tends to accumulate in sediments. Chemical oxidation technique is unable to oxidize all organic pollutants. Heterogeneous photocatalysis is widely studied method for the degradation of pollutants due to its low cost and potential to remove organic pollutants from waste water. Major advantage of this method is, complete degradation of organics into non hazardous CO_2 and H_2O. Titanium dioxide (TiO_2) based materials are widely used as promising photocatalytic material (Jafari et al., 2016; Lavand and Malghe, 2015a; Khan and Kim, 2009). ZnO has been reported as a suitable alternative to TiO_2 in view of the fact that its photodegradation mechanism is similar to that of TiO_2. In the past two decades, ZnO has attracted much attention with respect to the degradation of various pollutants due to its high photosensitivity, good optical properties, non-toxic, stability and wide band gap. ZnO is reflected as a low cost alternative photocatalyst to TiO_2 for degradation of organics in aqueous solutions. Main advantage of ZnO is that it can absorb a larger fraction of the solar spectrum than TiO_2 (Zaier et al., 2015; Hong et al., 2008), and hence ZnO photocatalyst is considered more suitable for photocatalytic degradation in the presence of sunlight (Pawar et al., 2013; Lavand and Malghe, 2015b). However, it can be activated using UV light only, which contributes approximately 5% of solar spectrum (Iqbal et al., 2016). Hence, many attempts have been dedicated to prepare visible light active ZnO photocatalyst. It can be achieved by doping of ZnO with transition metals and anionic non-metals. Among them, doping of ZnO with transition metal cations was reported as a good tool to improve photocatalytic properties for enhancement of visible light response (Bahsi and Oral, 2007). Fe doped ZnO nanocrystalline particles showed better photocatalytic activities than pure ZnO under visible light in many reports. It was believed that Fe(III) cations could act as shallow traps in the lattice of photocatalyst, which reduced the recombination rate of electron/hole. Best photocatalytic properties could be achieved upon doping iron at a relatively weak level. Additionally, doping with nonmetallic species, such as N, C, S, P and halogen atoms also caused the photosensitization of ZnO in the visible light region. Among various non-metal modified ZnO, carbon doped ZnO has been reported as a kind of promising photocatalyst (Lavand and Malghe, 2015c). Cho and co-workers reported that C doped ZnO prepared using vitamin-C was able to photodegrade Orange-II under visible light. Zhang et al. found C doped ZnO nanoparticles prepared by facile one pot synthesis exhibited high photocatalytic activity for degradation of methylene blue under visible light illumination. Haibo et al. synthesized C-doped ZnO by calcinations of powders prepared by hydrothermal reaction of zinc gluconate and this C-doped ZnO photocatalyst showed a good visible light activity for RhB decoloration. Carbon doping could create new energy state in the band gap as well as oxygen vacancies in the bulk of ZnO, which could be responsible for the visible photoactivity of C-doped ZnO. More recently, the simultaneous doping of two kinds of atoms into ZnO has attracted considerable interest, since it could result in a higher photocatalytic activity and peculiar characteristics compared with single element doping into ZnO. Hence, in the present work C and Fe co-doped ZnO nanostructures were synthesized using microemulsion method. Synthesized material was characterized using various characterization techniques and its visible light photocatalytic activity was investigated for the degradation of TCP.

2. Materials and methods

2.1. Chemicals

2,4,6-Trichlorophenol (TCP) used in the present study was procured from SD fine Chemicals Ltd. Mumbai, India and used without any further purification. Zinc nitrate ($Zn(NO_3)_2$. $6H_2O$) was obtained from Merck Chemicals, Mumbai, India and used as zinc source. AR grade cyclohexane, n-butanol, N,N,N-cetyl trimethyl ammonium bromide (CTAB), acetone, ferric nitrate ($Fe(NO_3)_3.9H_2O$), sodium hydroxide (NaOH) and ethanol were procured from SD Fine Chemicals Ltd. Mumbai, India and used without further purification.

2.2. Catalyst synthesis

Pure ZnO and C as well as C, Fe co-doped ZnO photocatalysts were prepared by microemulsion method. The detailed procedures are as follows: zinc nitrate (1 mol/L, 57.6 mL) and stoichiometric amount of ferric nitrate was added to a mixture of cyclohexane (71 mL), CTAB (11.8 g) and n-butanol (16 mL) with constant stirring for 20 min to obtain microemulsion A. Sodium hydroxide (2 mol/L, 57.6 mL), cyclohexane (71 mL), and CTAB (11.8 g) were mixed with n-butanol (16 mL) with stirring for 30 min to obtain microemulsion B. Microemulsion B was added drop wise to microemulsion A with constant stirring for 30 min. The resultant mixture was transferred to 250 mL stainless steel autoclave (with Teflon inner liner) and kept in an oven at 150 °C for 2 h. After, it was cooled to room temperature and the residue obtained was separated using filtration, it was washed several times with ethanol and water and dried in an oven at 40 °C. The product obtained was used as a precursor. This precursor was calcined in furnace at 300 °C for 2 h to get C, Fe co-doped ZnO. The iron doping concentration was chosen as 0.5, 1.0, 2.0, 3.0 and 5, which was the mole percentage of Fe(III) in the theoretical ZnO powder. C doped and pure ZnO were prepared using same method. During this preparation microemulsion A was prepared without adding ferric nitrate. Precursor obtained was calcined at 300 and 500 °C gave C doped and Pure ZnO respectively.

2.3. Characterization methods

Simultaneous TG and DTA curves of C, Fe co-doped ZnO precursor were recorded by heating 8.87 mg sample in nitrogen atmosphere with a constant heating rate 10 $°C\ min^{-1}$ using Rigaku TG-DTA system (Model-Thermo Plus TG8120). X-ray diffraction patterns (XRD) of the precursor calcined at 300 °C were recorded using X-ray diffractometer (Rigaku, Model-Miniflex II). FT-IR spectra of precursor and the precursor calcined at 300 °C were recorded using FT-IR