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Nano sized Fe doped strontium titanate for photocatalytic degradation of dibutyl phthalate under visible light

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ABSTRACT

Nano-sized $SrTiO_3$ and $SrTi_{0.7}Fe_{0.3}O_3$ photocatalysts were prepared by the complex route precursor method. The prepared photocatalysts were characterized by XRD, TEM, XPS and diffuse reflectance. The effect of iron doping on the structural properties and the photocatalytic activity was studied. All the prepared samples have single cubic perovskite structure. It was found that doping of $SrTiO_3$ with Fe shifted the peak positions toward higher 20 value, decreased both the cubic lattice parameter and the unit cell volume, decreased the average crystallite size of $SrTiO_3$ from 53 nm to 35 nm and shifted the absorption to the visible light range (red shift). The photocatalytic degradation activity of 30 mole % Fe doped $SrTiO_3$ was significantly improved the degradation of dibutyl phthalate in 90 minutes under visible light irradiation by 4 times higher than $SrTiO_3$. Copyright © 2016 VBRI Press.

Keywords: $SrTi_{0.7}Fe_{0.3}O_3$; wastewater treatment; photocatalysts; photodegradation.

Introduction

Perovskite-based compounds are interesting materials since their structures are very versatile and allow different and useful applications such as photocatalysis, oxygen sensors, anodes for solid oxide fuel cells, and mixed conductors for membranes used in oxygen extraction. Strontium titanate (SrTiO₃), as a photocatalyst, possesses wide band gap energy (Eg = 3.2 eV) and high stability in addition to wide potential application in water treatment [**1-3**]. SrTiO₃ (ST) is wide band gap semiconductor and acts as a photocatalyst in the UV light range. SrTiO₃ could be used in visible light by cation doping [**4-7**].

In the past, $SrTi_{1-x}Fe_xO_3$ (STF) solid solution attracted the attention of many researchers due to its potential as an oxygen gas and hydrocarbonates sensors for automotive emission control [8–14]. To the best of our knowledge, the photocatalytic activity for STF is not reported yet while it is a p-type conducting semiconductor material with the perovskite structure that could be used in oxygen sensor.

Dialkyl or alkyl aryl esters of 1, 2 - benzendicarboxylic acid (phthalic acid) are group of compounds called Phthalate esters (PAEs). Dimethyl phthalate (DMP), diethyl phthalate (DEP) and dibutyl phthalate (DBP) are the mostly used (PAEs) for variety of commercial purposes and have been listed as priority pollutants by agencies such as U.S. Environmental Protection Agency [**15-16**]. DBP is used in child care products, cosmetics and children's toys. It is not chemically bonded to the plastics polymer so they can eventually leach out from the plastics into water thereby posing serious risks to ecosystem components causing hepatotoxic, teratogenic and carcinogenic effects. DBP also reduces human sperm production and motility, decreases the rates of pregnancy and promote miscarriages [15, 17-19]. Therefore, researchers are focusing on BDP removal from water [20-21].

The main purpose of the present work is to synthesize of nano-sized ST and STF photocatalysts by the complex route precursor and studying the effect of Fe³⁺, having smaller ionic radius than Ti⁴⁺, doping on the structural properties, the band gap and the photocatalytic activity of ST. Moreover, the photocatalytic activity of ST and STF system for degradation of DBP as a model in aqueous solution will be evaluated.

Experimental

SrTiO₃ (ST) powder sample was synthesized by complex route precursor according to Wang *et al.* [**22**]. citric acid, tetra-n-butyl titanate Ti(n-OC₄H₉)₄, Sr(NO₃)₂, H₂O₂ (30 wt.% in H₂O), ammonia solution (25-28 wt.% in H₂O), were used as the starting materials. All chemicals were reagent grade and used as received.

Ti(n-OC₄H₉)₄ was added to stirred deionized water, precipitation and turbidity were observed gradually. The precipitate was filtered and washed for several times with deionized water. The precipitate was added to the citric acid solution with molar ratio of CA:M=2:1 (CA=citric acid and M=Ti) with stirring. 1 ml of H₂O₂ was then added and the pH value of the solution was adjusted to 6 using ammonia solution. The prepared yellow solution of Ti(IV) was stirred and refluxed at 60 °C. This solution is called solution (I). Citric acid was added to Sr(NO₃)₂ solution in a molar ratio of CA:M=2:1 (M=Sr) and the pH was adjusted to 6 using ammonia solution. This solution is called solution (II). Solution (I) was then mixed with solution (II) and the whole mixture was refluxed at 60 °C for 2h with continuous stirring. The precursor solution was heated at 90 °C in water bath with stirring till gel is formed. The obtained resin was dried at 90 °C then calcined with intermediate grinding at 500, 600, 700 and finally at 800 °C for 2 h.

STF powder samples was prepared using the same method mentioned above where Fe(NO₃)₃.9H₂O solutions was added to solution (II). The crystal structure was examined using X-ray diffraction (XRD). The XRD measurements were carried out using Empyrean diffractometer equipped with Cu radiation CuKa $(\lambda=1.54056 \text{ Å})$. The lattice parameters were determined using program called unit cell [23]. The crystallite size was calculated using program called winfit [24-25]. The microstructures were observed by a high resolution transmission electron microscope (TEM, JEOI JEM2100). The band gap was determined from diffuse reflectance measurements (Shimaduz UV-3600). Binding energy of the elements was measured at room temperature by X-ray photoelectron spectroscopy (Thermo scientific k-alpha Al DHA).

Experimental setup for degradation

A slurry mode batch reactor equipped with a cooling jacket was used for photocatalytic degradation reaction process. Commercial visible metal halide lamp (HQI-T 250/Daylight, OSRAM GmbH, Germany) with Luminous flux of irradiation 20,000 lm with luminous efficacy of 82 lm/W was used as source of visible light. The solutions as well as the catalyst were magnetically stirred. At different time intervals, a sample of 4 ml was taken from the reaction suspension then centrifuged to separate the solution and the photocatalyst.

DBP determination

DBP removal was measured by determination of total Organic Carbon (TOC) using TOC analyzer (Torch-Teledyne Tekmar) with accuracy of 99.9 %.

Results and discussion

Characterization

XRD was used to detect the crystal structure of the prepared samples. **Fig. 1** shows the XRD pattern for the prepared samples. It was clear that both $SrTiO_3$ (ST) and $SrTi_{0.7}Fe_{0.3}O_3$ (STF) samples have the cubic pervoskite like phase structure (JCPDS 84-0443). There is shift to higher theta value as a result of doping of $SrTiO_3$ by Fe as shown from the inset of **Fig.1**. The intensity of STF XRD peaks is smaller than that of ST sample. The decrease in the crystallite size in case of Fe doping is consistent with Jamil et al work [**26**] where it was noted that the larger the amount of Fe^{3+} doping, the wider the width of the diffraction peaks, the worse the crystallization, and the smaller the grain size of TiO₂ powders.

The calculated cubic lattice parameter, cubic unit cell volume and the average crystallite size for the prepared samples are presented in **Table 1**. Doping of ST by Fe decreased both the cubic lattice parameter and unit cell volume.



Fig. 1. The XRD pattern of the prepared ST and STF samples. The inset shows the 110 peak expansion.

This might be due to the substitution of the larger Ti^{4+} ion (ionic radius= 0.605 pm [27]) by the smaller Fe³⁺ ion (ionic radius=0.58pm [27]).

Table 1. Microstructural parameters of ST and STF samples.

Sample	a (Å)	V (Å ³)	Average crystallite size (nm)
ST	3.90411	59.5067	53
STF	3.90228	59.4232	35

The diffuse reflectance spectra were transformed to absorption spectra according to the Kubelka–Munk relationship to evaluate the band gap for the prepared samples. The diffuse reflectance of ST and STF samples was presented in S.1 in the Supplementary information. The inset of S.1 shows the diffuse reflectance of STF sample. From S.1 it is clear that the undoped ST sample shows absorption edge at 398 nm which corresponds to band gap of 3.12 eV. Doping ST with 30 mole% of Fe decreased the absorption edge to 520 nm and accordingly the band gap to 2.38 eV. Both the red shift and the reduction in the band gap might be due to the new energy states introduced by Fe ion between the conduction band and the valence band as illustrated in the Supplementary information S.2.

S.3 in the Supplementary information shows the TEM of STF sample. The particles showed irregular shape with noticeable agglomeration of the particles.

Fe XPS spectra for STF sample were presented in **Fig. 2** to detect the oxidation state of Fe. It is clear that the XPS spectra exhibit two signals of $Fe2p_{1/2}$ and $Fe2p_{3/2}$. The peak position of $Fe2p_{1/2}$ corresponds to that of Fe^{3+} ion [**28**].

Photocatalytic degradation

Photocatalytic activity of ST and STF nanoparticle samples were examined by photocatalytic degradation of DBP at

initial concentration of 50 mg/L, pH 3 and 0.75 g/L of catalyst.



Fig. 2. XPS spectra of Fe 2P of STF sample.

Fe doped ST (STF) shows higher removal for DBP than ST itself as shown in Fig. 3. This can be attributed to substitution of Ti⁴⁺ in the crystal structure of titanate by Fe⁺³, this is proved by peak shifting in XRD pattern (**Fig. 1**) as well as the lattice parameter and unit cell volume values of ST and STF samples (Table 1) i.e., introduction of new Fe level that can be used as intermediate stage between conduction band (CB) and valence band (VB) of ST. Accordingly, electron can be promoted from VB to CB through introduced Fe level resulting in narrower band gap than naked ST increasing the absorption in visible light region [26]. Subsequently, adsorbed oxygen and hydrogen peroxide reacts with the departed electrons and migrated holes respectively on the surface of the catalyst forming and which are responsible for photodegradation of DBP [29]. Stability in irradiation time was noticed at 90 min. indicating that it is the optimum reaction time.



Fig. 3. Photocatalytic degradation of DBP under visible light.

Due to very low removal with ST, the other optimum conditions such as pH, catalyst dosage and kinetics were studied to STF only pH value of the solution plays an important role in photocatalytic degradation of DBP [**30**]. Electrostatic interaction between DBP and the prepared

photocatalysts will be affected due to changing the initial pH value of the solution since, the potential of redox reaction affecting the reactivity of organic solutes [**31**]. The effects of pH on photodegradation performance of the prepared photocatalysts were therefore evaluated.

The initial pH of 50 ppm DBP without any adjustment was found to be 6.9 in the deionized water solution. The effect of pH on the degradation of DBP by the prepared photocatalysts is presented in **Fig. 4** with catalyst dose of 0.75 g/L, contact time 90 min and initial DBP of 50 mg/L. As the pH is increased the degradation rate increases, reaching a maximum at around pH = 9. However, the degradation activity of DBP decreases gradually when the pH exceeds 9 (**Fig 4** insert). The results can be explained by the recognized effects of pH on surface charge of catalyst and pollutants, absorption of contaminants on surface of the photocatalyst, and hydroxyl concentration, which ultimately affect the degradation efficiency [**32**].



Fig. 4. Effect of pH on DBP removal by $SrTi_{0.7}Fe_{0.3}O_3$, Insert: DBP removal as function of pH.

For an amphoteric material such as STF, the change in the concentrations of H⁺ and OH can affect its net surface charges. Apparently, the increasing degradation rate with pH 9 could be attributed to the fact that in alkaline media, a higher level of hydroxide ions (OH⁻) induced the generation of hydroxyl free radicals (OH) as shown in equations (1-6). The formation of hydroxyl free radicals occurs from photo oxidation of OH by holes formed on the surface of the photocatalysts [33]. Since hydroxyl free radicals are the primary oxidizing species in degradation of DBP, the rate of degradation is increased as the pH of the solution is increased. However, as the pH is increased beyond the ideal point the degradation decreases, this is because the pollutant and catalyst molecules at higher pH repel, lowering the absorption of DBP on the surface of photocatalyst, which is known to lead to poor photochemical degradation [34].

Catalyst + hv (λ >400nm) \rightarrow Catalyst (ecb-+ hvb) Catalyst (ecb-) + O ₂ \rightarrow Catalyst + o_2^-	
$e^+ O_2 \rightarrow o_2^- \rightarrow H_2 O_2 \rightarrow 2OH.$	(4)
h_{vb+} + pollutant \rightarrow degradation product	(5)
o_2^- + Pollutant \rightarrow degradation product	(6)

It can be noticed in **Fig. 5** that as catalyst dosage is increased from 0.25 g/L to 1.25 g/L, the activity also increases up to a catalyst dosage of 1.0 g/L then starts to decrease at catalyst dosage 1.2 g/L. So, maximum removal was observed at 1.0 g/L catalyst dose with 90 min irradiation time. Increase of catalyst load will lead to increase in electron/hole pair due to increasing the number of available active sites accordingly, amount of hydroxyl radicals produced will be increased, and thus the photocatalytic activity is enhanced [**35-36**].

However, photocatalytic activity is reduced by increasing the catalyst loading after optimum dose (1.0 g/L) as shown in **Fig. 5** insert due to higher extent of light scattering which negatively impacts light penetration [**37-38**].



Fig. 5. % removal of DBP by x = 0.01 sample as a function of catalyst dose at different time. Insert: DBP removal a function of STF dosage.

In order to establish the dependence of removal efficiency on the pollutant concentration, solutions of different initial concentrations of DBP were degraded using STF and amount of photocatalyst, 1 g/L of each separately. The results shown in **Fig. 6** showed that degradation of DBP by STF obeys pseudo first order equation which indicates linear relationship between Ln Ct/C0 versus time as shown in equation (7).

$$\operatorname{Ln} C_t / C_0 = kt \tag{7}$$

where, C_0 and C_t are the concentrations of DBP at t = 0 and t, respectively and k is the rate constant.

Also, **Fig. 6** indicated that the activity of the photocatalyst decreases with increasing concentration (10-25 mg/L). The relationship between DBP concentration and photocatalytic activity is associated with the absorption of DBP on the surface of STF [**39**]. Therefore, increasing DBP concentration decreases activity due to the limitation of the number of active sites available for DBP molecules on STF surface [**40**]. Also with increasing DBP concentration, more and more organic intermediates compete with hydroxyl ions for absorption at the active sites of STF, thus reducing the generation of hydroxyl radicals [**37**, **41**]. The previous results can be confirmed by

decreasing k values with increasing DBP concentration as shown in **Fig. 6** insert.



Fig. 6. Pseudo first order kinetic for different DBP doses with STF, insert: correlation between k value and DBP concentration.

Conclusion

As a result, in this manuscript, complex route precursor technique was used for preparation of nano-sized SrTiO3 as well as SrTi_{0.7}Fe_{0.3}O₃ photocatalysts. The prepared photocatalysts were fully characterized. Their photocatalytic activity was confirmed by degradation of DBP. SrTi_{0.7}Fe_{0.3}O₃ has the higher photocatalytic activity than naked SrTiO3. Since, it has 50 % degradation of DBP in 90 min under visible light which is much higher than SrTiO3 before optimization. The percent removal of DBP by SrTi_{0.7}Fe_{0.3}O₃ was around 88 % under optimum reaction conditions which are 90 min irradiation time, 1.0 g/L catalyst dosage at pH 9 taking in consideration that the initial concentration of DBP is 50 mg/L. Also, the reaction kinetic was pseudo first order kinetic. Accordingly, doping of SrTiO₃ with Fe increased the photocatalytic activity under visible light which is ensured by appearance of red shift at 520 nm by UV-Vis absorption corresponding to band gap of 2.38 eV which is higher than that of SrTiO₃ (392 nm) corresponding to band gap of 3.12 eV.

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Supporting information



S. 1. Diffuse reflectance spectra of ST and STF samples. The inset shows the diffuse reflectance of STF sample alone.



S. 2. Schematic illustration for the calculated band gap for the prepared samples and also the new energy levels introduced by Fe ion.



S. 3. The TEM image of STF sample.