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Tuning effect of Sn doping on structural, morphological, optical, electrical and photocatalytic properties of iron oxide nanoparticles

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ABSTRACT

The pure and tin-doped iron oxide nanoparticles were synthesized by using the microwave irradiation method by varying the different wt% of Sn. Samples with better quality were prepared using 0.1 mol of Hexadecyl trimethyl ammonium bromide (HTAB) as surfactant. The influence of Sn levels lead to change in morphology of rhombus shaped platelets at lower doping levels of Sn into spherical shaped particles at higher doping levels. The respective change due to the Sn wt% in iron oxide was also altered the particle size, which was verified with the help of XRD and HR-TEM studies. The diffusion of Sn in an iron oxide lattice by incorporating Fe^{3+} sites were confirmed with the help of XPS spectrum. The electrical conductivity change was observed due to Sn doping levels in iron oxide. The tuning of bandgap variations on electrical conductivity was confirmed due to decrease of conductivity of higher doping level of Sn in iron oxide nanoparticles. The bandgap of iron oxide nanoparticle was tuned from 2.21 eV to 2.44 eV due to the incorporation of Sn in an iron oxide lattice. The change in band gap energy due to this reason is highly influenced on degradation of methylene blue dye. Photocatalytic activity under sunlight is clearly identified by the degradation.

1. Introduction

Iron oxide is the n-type semiconductor, which possess less band gap energy. Generally it is considered as environmentally friendly oxide which attracts the researchers on using the iron oxide in different microelectronics device fabrications. The α-Fe_2O_3 phase of iron oxide is simply termed as Hematite [1]. The iron oxide in nanorange creates high impact on change in physical properties. Nowadays, the change in properties of iron oxide (α-Fe_2O_3) nanoparticles can be observed by doping of semiconductor material [2]. There are enormous numbers of techniques followed by researchers for synthesis of iron oxide nanoparticles. The synthesis method played a significant role on creating the property change. Iron oxide nanoparticles can be used in the different applications such as, photoanode [3], solar water splitting [4,5], solar cell [6], gas sensors [7–9], photocatalysts [10,11]. Also the property of the iron oxide nanoparticle is further altered by doping of different metals [12,13]. The concept of doping of different metal in iron oxide was done to alter the properties of iron oxide nanoparticles [14]. The incorporation of metals such as Si, Ni and Sn can be done by different preparation methods, such as hydrothermal [15], solid state reaction [16], cationic substitutions [17], Among these synthesis process, the present work is focused towards microwave irradiation. This process is a unique one on preparing Sn doped in iron oxide (α-Fe_2O_3) nanostructures and so far no researchers have attempted on microwave irradiation technique with HTAB as surfactant. The occurrence of morphological change due to both microwave irradiation and surfactant role is also well identified from this study. The tuning effect of the bandgap energy has been identified from the different doping level of Sn in iron oxide. The method of microwave irradiation process with surfactant is also supported for platelet formation at specified Sn concentration.

Among different metal oxide materials, iron oxide (α-Fe_2O_3) has attracted much attention due to its favorable optical band gap (2.2 eV) [18] as well as its chemical stability in oxidative environment. Because of the Sn doping in iron oxide is improved the structural, electronic and optical properties of iron oxide. In which the doping of tetravalent Sn^{4+} dopant can be doped into iron oxide at the Fe^{3+} sites. This article also focused on, change in bandgap of Sn-doped iron oxide nanoparticles due to their different weight percentage of Sn such as such as, 10, 20, 30, 40 and 50 weights (wt) percentages (%) respectively. The influence of Sn doping on iron oxide nanoparticles is also created a change in particle size and morphology [19]. This microwave irradiation process is much supported to change the morphology which will tune the bandgap and change its electrical conductivity. The main advantages of microwave irradiation assisted organic synthesis process are, accelerate the rate of reaction, provide better yields, higher purity,

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energy saving, uniform and selective conventional heating with lower energy usage, help in developing convenient and cleaner synthetic routes. The use of microwaves has also reduced the amount of purification required for the end products of chemical reactions and consequently the reactions are completed in few minutes instead of hours. The resulted product further annealed at 400 °C. The annealing process is an important role on metal oxide nanoparticles to induce the phase change from amorphous to rhombohedral and the surface of the iron oxide and agglomeration growth of the nanoparticles. The photocatalytic activity also tested with pure and Sn doped iron oxide nanoparticles. In earlier, Zhigin Cao et al. [20] have studied the photocatalytic activity for low doping of 3–8% of Sn in iron oxide. The degradation has been studied with the help of hydrogen peroxide (H_2O_2) as oxidant and irradiated by commercial 250 W halogen lamps. But in our work degradation effect for the samples are tested under the sunlight and without H_2O_2 oxidant.

2. Experimental details

The chemicals used for the preparation were of analytical grade iron (III) Chloride anhydrous [$FeCl_3{\cdot}2H_2O$-Merck], tin (II) chloride dihydrate ($SnCl_2$) -Merck, hexadecyl trimethyl ammonium bromide (HTAB) ($CH_3(CH_2)_{15}N(CH_3)_3Br$-Alfa Aesar) and Ammonium Hydroxide [NH_3 OH-Merck].

2.1. Synthesis method

The iron oxide nanoparticles are formed with various sizes and shapes by microwave irradiation process. This method has specific advantages like simple, cost effective and high yield. The respective process for synthesis of pure and Sn doped iron oxide nanoparticles are discussed below. The microwave irradiation process was adopted for the preparation of Sn doped iron oxide nanoparticles. The microwave radiation frequency was used for synthesis as 2.41 GHz. The 0.1 mol solution was prepared by dissolving 90% of iron (III) chloride anhydrous ($FeCl_3$) in 100 ml deionized water. The remaining 10 weight percentage of Sn doping was done by dissolving 10% weight of tin (II) chloride dihydrate ($SnCl_2$) in 100 ml deionized water. Further, the hexadecyl trimethyl ammonium bromide (HTAB) of 0.1 weight percentage from total weight was dissolved in 50 ml deionized water. All the prepared solutions were stirred individually for 1 h. The iron chloride ($FeCl_3$) solution was added drop by drop in the medium of HTAB solution by using a burette. In a similar way without altering the stirring condition $SnCl_2$ solution was added again drop by drop in the previous solution. The mixed solution was stirred for 4 h at 70 °C. The pH of the solution was maintained at 8 by adding the 4 N normality concentration of ammonium hydroxide solution. In addition of ammonium hydroxide used to precipitate the solution. The resulting product washed for 15 times with double distilled water. Finally, precipitate was irradiated by microwave for 15 min. The irradiated yield was further annealed at 400 °C for five hours. The similar synthesis procedure repeated for other doping level of Sn in iron oxide nanoparticles, such as 20 wt%, 30 wt%, 40 wt% and 50 wt% of Sn.

The pure iron oxide nanoparticles were prepared by the microwave irradiation process. The 0.1 mol of iron chloride ($FeCl_3$) taken into 100 ml of double deionized water. The 0.1 weight percentage of HTAB was prepared in 50 ml solution as surfactant solution. The prepared precursor $FeCl_3$ solution added drop by drop in the surfactant solution. The pH of the solution was maintained at 8 by adding ammonium hydroxide solution. After adding reagent, the solution was precipitated and precipitation is irradiated by using microwave radiation for 15 min. The yield obtained after microwave irradiation process is further annealed at 400 °C. The prepared samples are named such as, pure iron oxide nanoparticles as the sample (a), 10 wt% of Sn doped iron oxide nanoparticles as the sample (b), 20 wt% of Sn doped iron oxide nanoparticles as the sample (c), 30 wt% of Sn doped iron oxide nanoparticles as the sample (d), 40 wt% of Sn doped iron oxide nanoparticles as the sample (e) and 50 wt% of Sn doped iron oxide nanoparticles as the sample (f) respectively.

2.2. Experiment for degradation of methyl blue (MB) dye

The photocatalytic activity undoped pure iron oxide (sample (a)), 10 wt% of Sn doped iron oxide (sample (b)), 20 wt% of Sn doped iron oxide (sample (c)), 30 wt% of Sn doped iron oxide (sample (d)), 40 wt% of Sn doped iron oxide (sample (e)) and 50 wt% of Sn doped iron oxide (sample (f)) nanoparticles were investigated by the degradation of methylene blue in aqueous medium under sunlight. In a typical photocatalytic experiment, 75 mg of undoped and Sn doped iron oxide nanoparticles were added to the 100 ml aqueous methyl blue solution. The irradiation was done by loading the samples in quartz tube and kept them in open sunlight. The concentration of MB dye prior to irradiation was recorded to analyses the initial value by UV spectrum. The irradiation on the solution is recorded for every five minutes interval. The radiation is measured continuously until the decolourization of the solution. The percentage of efficiency was calculated at end of decolourization by using the following formula,

$$\text{Decolourization efficiency}(\%) = \frac{(\text{Absorption})o-(\text{Absorption})t}{(\text{Absorption})o} x100$$

Where, $(\text{Absorption})_O$ is the absorbance before irradiation of MB dye and $(\text{Absorption})t$ is the final concentration of MB dye after irradiation. Analysis with a UV–Vis spectrometer showed degradation of the dye was seen decolourization over time in the presence of the Sn doped iron oxide.

2.3. Characterization

The structure of the Sn doped iron oxide nanoparticles was analyzed by X-ray diffraction pattern (XRD) using Rigaku X-ray diffraction unit model ULTIMA III. The iron oxide nanoparticle characterized by Fourier Transform Infrared (FT-IR) spectrum was recorded by using a JASCO FP-8300, Japan IR spectrometer. The optical studies of Photoluminescence spectrum (PL) recorded by JASCO FP8300, Ultraviolet (UV–visible DRS) absorption spectrum was also recorded by using JASCO V-770 Spectrophotometer. The morphology and size of the products were observed by High Resolution Transmission Electron Microscopy (HR-TEM) and Selected Area Electron Diffraction (SAED) was recorded from the samples by using Technai G20-stwin an accelerating voltage of 200 kV. The elemental presence of Sn doped iron oxide powder was confirmed by using Energy Dispersive X-ray analysis (EDAX) an accelerating voltage of 15 kV with Field emission scanning electron microscope (FE-SEM) by Zeiss ultra plus, the dopant were confirmed by X-ray photoelectron spectroscopy (XPS) measurements with an SSX-100 spectrometer equipped with a focused spot size 600 Å monochromatised Al Kα $h\upsilon - 1486.6$ eV. The electrical conductivity was predicted by using Keithley 6517B Electrometer. The whole Microwave irradiation process was carried-out by IFB (Model:17PM-MEC1) Microwave Oven.

3. Results and discussion

3.1. XRD analysis

The microwave treated pure iron oxide nanoparticles and Sn doped iron oxide nanoparticles under different weight percentage of Sn dopants are analyzed by X-ray diffraction pattern and it is shown in Fig. 1(a-f). This XRD pattern represents pure iron oxide and the different doping percentage level of Sn in iron oxide nanoparticles samples such as, sample (a), sample (b), sample (c), sample (d), sample (e) and sample (f) respectively. The corresponding peaks referred the Miller indices of iron oxide nanoparticles of sample (a) such as (012) (104)