Research Article

Novel Preparation of Fe Doped TiO₂ Nanoparticles and Their Application for Gas Sensor and Photocatalytic Degradation

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The preparation of Fe doped TiO₂ is demonstrated as well as application for gas sensing and photocatalytic degradation. Fe doped TiO₂ nanopowder was prepared by the mechanochemical ball milling method. The results show the uniform doping of Fe in TiO₂ powder. The average size of the particle is observed to be ~28 nm. The H₂ gas sensor was fabricated using the Fe doped TiO₂ nanopowder and the effect of Fe doping on the sensing properties is investigated with various temperature ranges. The prepared Fe doped TiO₂ nanoparticles are also used to explore degradation properties of Rhodamine B dye under LED light.

1. Introduction

Titanium dioxide (TiO₂) is a well-known multifunctional metal oxide material because of its wide range of applications and benign properties such as stability and nontoxicity [1]. The wide range of uses of TiO₂ is due to its unique electronic and structural properties. TiO₂ exists in three main crystallographic forms: anatase, rutile, and brookite. However due to high band gap of TiO₂ (>3 eV) its optical application is limited to UV region of the electromagnetic spectrum [2]. Doping opens up the possibility of changing the electronic structure of TiO₂ nanoparticles, altering their chemical composition and optical properties. Much effort has been made by incorporating doping with metal ions, such as nickel, chromium, iron, vanadium, and zinc [3–7].

Iron metal ions have been considered as a suitable candidate, for doping owing to the fact that the radius of both Fe³⁺ (0.64 Å) and Ti⁴⁺ (0.68 Å) is similar in size. Therefore, it can be easily incorporated with the crystal lattice of TiO₂ [8]. One of the advantages of inclusion of Fe into TiO₂ lattice is its potential application in photocatalysis and hydrogen production due to reducing in the energy gap of TiO₂ and increasing the efficiency of absorbing visible light [9]. However, the application of Fe doped TiO₂ for gas sensing, especially hydrogen sensing, has still not been properly explored. It is also well recognized that doping Fe can improve the grain size, carrier concentration, and thermal stability of the TiO₂ sensor performance significantly. Furthermore, several researchers reported about the fabrication of Fe doped TiO₂ using the spin coating method Effendi and Bilalodin, reported the Fe doped TiO₂ powder using Titania and iron oxide as chemical precursors [10]. Kumar et al. reported the fabrication of Fe doped TiO₂ film by sol-gel technique for the application of gas sensor [11]. Othman et al., reported the Fe doped TiO₂ nanoparticles produced by MOCVD method for photocatalytic activity [12]. However, there are very few reports of preparing Fe doped TiO₂ nanoparticles by the mechanochemical ball milling method. Carneiro et al. studied the effect of Fe on TiO₂ powder on optical and photocatalytic properties [13].

In this work, we have developed Fe doped TiO₂ nanopowder using mechanochemical ball milling method. The effect of the ball milling procedure on Fe doping in TiO₂ is systematically studied. H₂ gas sensor was fabricated using the prepared powder and sensing properties are studied.

2. Experimental Procedure

Iron doped TiO₂ nanoparticles were prepared by ball milling of TiO₂ powders (TiO₂ P25) in a high-energy ball mill in the
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Figure 1: The pH variation during ball milling process.

presence of fine FeCl₃ powder using Al₂O₃ balls. The slurry was prepared by mixing TiO₂ powder and iron chloride in DI water in 1:5 ratio for 120 min at 1200 rpm. After 30 min the Ag powder was added in the slurry for the removal of unreacted FeCl₃. The slurry was monitored by pH meter. After reaction the slurry was washed with DI water and ethanol for removing the impurities. Finally, the powder was dried at 80°C in an open atmosphere.

3. Results and Discussion

Initially, the TiO₂ and FeCl₃ powders were mixed in DI water. The pH of the slurry changed to acidic medium with value 1.8. This indicates iron chloride dissolution in water and formation of iron hydroxide, as shown in (1) in the following:

FeCl₃ (s) + H₂O (excess) → Fe³⁺ (aq) + 3Cl⁻ (aq)  \hspace{1cm} (1)

2Fe³⁺ (aq) + 6H₂O → 2Fe(OH)₃ (s) + 6H⁺ (aq) \hspace{1cm} (2)

The pH of the slurry remained steady for 30 min ball milling. To remove the Cl⁻ ions from the slurry Ag metal powder was added and the slurry was ball milled for another 30 min. During this time pH of slurry was increased gradually from 1.8 to 4.5 as shown in Figure 1. The experimental flow chart of fabrication of iron doped TiO₂ nanoparticles is shown in Figure 2. It is also noticed that amount of Fe dopant concentration in the TiO₂ slurry is very important for the controlling the pH and size of the particle. Increase in the concentration ratio of FeCl₃ to TiO₂ will lead to more lattice distortion in the crystal. It causes a decrease in the crystalline density, yielding an increase in the size of the nanoparticles. To characterize the surface area of the Fe doped TiO₂ nanoparticles BET measurement was used. The BET surface area obtained was 51.856 m²/g and the total pore volume and average pore size were 0.462 cm³/g and 357.246 Å, respectively. It was noted that the surface area decreased with increasing in the annealing temperature of the powder. Table 1 shows the surface area, pore volume, and pore size of Fe doped TiO₂ at different annealing temperature.

Figure 3 shows the X-ray analysis of pure TiO₂ and synthesized Fe doped TiO₂ particles. The XRD profiles relieves the anatase phase (JCPDS number 84-1157) for pure TiO₂ and additional peaks of AgCl (JCPDS number 71-5209) for the doped sample as shown in the figure. All the peaks correspond to the (1 0 0), (0 0 4), (2 0 0), (1 0 5), (2 1 1), and (2 0 4) planes of anatase TiO₂. It is observed that the intensity of anatase phase in iron doped TiO₂ particles decreased with
Table 1: The surface area, pore volume, and pore size of Fe doped TiO$_2$ at different annealing temperature.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>BET surface area</th>
<th>Total pore volume</th>
<th>Average pore size</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>51.856 m$^2$/g</td>
<td>0.462 cm$^3$/g</td>
<td>357.246 Å</td>
</tr>
<tr>
<td>400</td>
<td>50.514 m$^2$/g</td>
<td>0.455 cm$^3$/g</td>
<td>367.671 Å</td>
</tr>
<tr>
<td>500</td>
<td>43.288 m$^2$/g</td>
<td>0.338 cm$^3$/g</td>
<td>334.475 Å</td>
</tr>
<tr>
<td>600</td>
<td>23.132 m$^2$/g</td>
<td>0.071 cm$^3$/g</td>
<td>136.759 Å</td>
</tr>
</tbody>
</table>

Figure 4: FESEM images of Fe doped TiO$_2$ (a) low magnification and (b) high magnification and (c) EDS spectrum table of the Fe doped TiO$_2$ particle.

FESEM images of Fe doped TiO$_2$ powder obtained after annealing at 450°C for 1 hour are shown in Figures 4(a) and 4(b). The avg. diameters of the nanoparticles are ~28–30 nm. The nanoparticles are of uniform size and spherical shape. It is noticed that agglomeration of particles increases with the annealing temperature. Figure 4(c) shows the EDS spectrum of Fe doped TiO$_2$ nanoparticles. The peaks of titanium and iron can be clearly seen in the spectrum with a dotted spot in the FESEM image. From the spectrum table, we can see the Fe (at. % 0.53) in the TiO$_2$.

Gas sensing measurement was performed with sensor fabricated by Fe doped TiO$_2$ for the detection of H$_2$ gas. Figures 5(a) and 5(b) show schematic diagram of sensor fabrication and illustration of hydrogen sensor measurement instrument. The sensor was prepared by coating the paste of nanoparticles powder on precoated Pt electrode alumina substrate. Initially 500 ppm of H$_2$ reducing gas diluted with nitrogen was used as the source gas. The typical dynamic
Figure 5: (a) Schematic diagram of sensor fabrication and (b) shows the schematic illustration of hydrogen sensor measurement instrument.

Figure 6: (a) Sensitivity plot at different operation temperatures 170, 220, and 270°C. (b) Dynamic responses from the sensor fabricated using Fe doped TiO$_2$ sample under the exposure of 500 ppm H$_2$.

Responses of sensor upon exposure to 500 ppm H$_2$ (Figure 6(a)) diluted in nitrogen were measured at different operating temperature of 170, 220, and 270°C. TiO$_2$ shows typical gas sensing behavior of n-type semiconductor where first the resistance of the sensor increases the operating temperature and decreases upon exposure to the H$_2$ gas [15–17].

A plot of the sensitivity to 500 ppm H$_2$ concentration measured as a function of operating temperature is shown in Figure 6(b). The effect of temperature on sensitivity of sensor on the H$_2$ response was higher with an increase in temperature. A significant increase of the H$_2$ response was observed at 270°C. The sensitivities of 68.1, 84.7, and 94.5 were observed at temperatures of 170, 220, and 270°C, respectively. It is also noticed that at lower temperatures 170 and 220°C sensor took longer time to stabilize to normal state after H$_2$ gas is off. At 270°C sensor recovers fast due to rapid desorption from the surface of nanoparticles.

The H$_2$ gas sensing mechanism of the resistive sensor base on metal oxide semiconductors was proposed in previous reports [18–20]. In current measurement (temperature range 160°C < $T_{substrate}$ < 270°C), the O$^-$ and O$_2$- oxygen ions are the dominant species on the surface of metal oxide semiconductors. The oxygen ions species extract electrons from the conduction of TiO$_2$. Thereby resistivity of the sensing layer increases and reaches steady state and when the H$_2$ gas is purged in; electrons are injected back to the conduction band thereby decreasing in resistance. In our case, sensing properties depend on the large surface area of the separated Fe doped TiO$_2$ particles, which provide more adsorption-desorption sites of gas molecules leading to improve the interaction between H$_2$ gas and adsorbed oxygen ions and thereby higher sensitivity was achieved.

The photodegradability of Rhodamine B dye solution was done using Fe doped TiO$_2$ powder. The solution was prepared by dissolving 0.2 g of Fe doped TiO$_2$ powder into 50 ml of 1 ppm concentration Rhodamine dye. Initially the solution was stirred for 30 min under dark to ensure complete surface adsorption of Rhodamine B onto the nanoparticles. After that LED white light was illuminated on the solution, for every 10 min samples were taken for checking the degradation property. Figure 7(a) shows the UV-Vis spectra of the dye solution with different interval time interval. The spectra data clearly demonstrates the photocatalytic efficiency of Fe doped TiO$_2$ powder in decolorization of Rhodamine B from pink to white under 60 min time interval. The gradual decrease
in the concentration ratio from initial to final decoloration is plotted in Figure 7(b). The photocatalytic mechanism of TiO_2 under UV light is well documented [21, 22]. Under the illumination of LED light, the pair of electron and hole released react with water and the electron-hole pairs migrate to the catalyst surface where they participate in redox reactions with adsorbed dye species. The holes (h^+) in valance band react with surface-bound H_2O to produce the hydroxyl radical and (e^-) in conduction band react with oxygen to generate superoxide radical anions. The formed hydroxyl radical (\*OH) and superoxide radical anions (O_2^-) degrade the pollutants in the photocatalytic oxidation processes. In our case, doping of Fe into TiO_2 enhances the electron-hole pair density thereby increasing the concentration of hydroxyl radical (\*OH) and superoxide radical anions thereby showing efficient catalytic reaction.

4. Conclusions

In this study, Fe doped TiO_2 nanopowder is prepared by the mechanochemical ball milling method. The prepared powder was characterized by using field emission scanning electron microscope (FESEM) and X-ray diffraction studies. The results show the uniform doping of Fe in TiO_2 powder. The avg. size of the particle is observed to be 28 nm. The H_2 gas sensor fabricated using the Fe doped TiO_2 nanopowder shows high sensitivity of 86% and it was noticed that sensitivity depends on the temperature. Also the effect of Fe doping on photodegradation of Rhodamine B under LED light was investigated. The results show that doping helps in decreasing degradation time lower than 60 min.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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