H₂ PRODUCTION FROM SULFIDE WASTEWATER USING ZnO DOPED TiO₂ PHOTOCATALYSIS

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Abstract - ZnO-TiO₂ powder synthesized with sol-gel method was used for production of hydrogen from sulfide wastewater. SEM, XRD, UV-DRS, FT-IR were used for characterization of the product. SEM shows that agglomeration of particles was due to cerium. XRD pattern indicates that crystal is tetragonal, body centred cubic lattice in anatase phase with particle size of 34.06 nm. The band gap energy of 1.7 eV and threshold wavelength of 700 nm were found using UV-DRS. Also, the surface adsorption was determined using FTIR. The photocatalytic properties for the production of H₂ from simulated sulfide water were studied using ZnO-TiO₂ a tubular photocatalytic reactor. The results show that 0.1 g suspended in 500 ml of simulated wastewater (10000 mg/L) irradiated at 150W visible lamp produced maximum H₂ of 5189 µmol h⁻¹ by converting sulfide (200 mg/L). The comparison of performance also reveals that ZnO-TiO₂ was better than Nano TiO₂ and TiO₂.

Key Words: ZnO-TiO₂, Band gap, Sulfide, Hydrogen, Photocatalysis, Sol-gel method.

1.INTRODUCTION

During the past few decades, refining crude oil by refiners have significantly reduced sulfur dioxide emissions in the transportation sector. The sulfur present in the crude oil is removed and it generates sulfide rich wastewater which is the biting issue in the industrial sectors. The presence of sulfide in the wastewater exerts a high biological oxygen demand of 2mol O₂/L mol S² which remains a threat to living organisms in water (Poulton et al., 2002). Hence, if released to the water bodies without treatment can cause serious environmental effects causing adverse threat to the aquatic life and mass fish mortality (Altas and Buyukgungor, 2008). Considering the impacts, the treatment of sulfide from wastewater is often attempted through various treatment processes like adsorption, coagulation, chemical oxidation, wet air oxidation, membrane technologies, and biological processes to avoid the related environmental concerns but all of them are either expensive or not friendly to environment (El Naas et al., 2009, Demirci et al., 1997, Abdelwahab et al., 2009, Sun et al., 2008, Rahman and Al Malack, 2006). Furthermore, refineries are also in need of large quantities of hydrogen to purify sulfur rich crude oils (World diesel, 2003). To resolve both the problems by framing a suitable strategy, solar photocatalysis is the best and beneficial treatment process which has a high oxidation potential (estimated to be +2.8V) to mineralize all the organic pollutants and the catalyst itself is non-toxic, cost effective and readily available (Al-Rasheed, 2005, Laoufi et al., 2008, Gaya and Abdullah, 2008). Among the semiconducting materials, more attention is given to TiO₂ because of its high photocatalytic activity, resistance to photocorrosion, photostability, low cost and non toxicity. Nevertheless, Titania has a large band gap (3.2 eV for anatase TiO₂) and therefore small fraction of solar light, about 2-3 % in the UV region can be utilized so that they cannot be installed in refineries to solve the problem. Hence, continuous improvement of photoreaction rate and the solar efficiency via adjusting the band structure of TiO₂ is a promising phenomenon at this stage.

To achieve this goal, metal doped titania is given more focus, testing their efficiency by comparison with pristine TiO₂ (Sampath et al., 1994 and Ranjit et al., 1997). So far, this technology is yet to be commercialized because of the low photocatalytic rate degradation efficiency on the surface of TiO₂ particles, which is due to the fast recombination rate of photogenerated electron-hole pairs. In order to slow
down this process and enhance the interfacial charge efficiency, the properties of TiO₂ particles have been modified by selective surface treatments, such as surface chelation, surface derivatization, platinization and doping of TiO₂ by certain metal ions. (Moser et al., 1991, Hong et al., 1987, Serpone and Lawless, 1994, Lin et al., 1998). In this perspective, many reports using transition metal ion or noble metal as dopants in TiO₂ system have come to the fore. Until last decade, transitional metals are used only in displays and lightings (Zhang et al., 2010 and Eliseeva et al., 2010) but it attained a new rise in the 21st century because of its afterglow property (Huangming et al., 2007, Yan et al., 2010, Mitsuo et al., 2009).

To impart the efficiency in catalytic activity, doping of foreign transition elements into the existing photocatalysts (cationic doping) is one approach and has been studied extensively (Mills et al., 1997, Kato et al., 2002, Ishii et al., 2004). Another approach to synthesize active visible light catalyst is to dope oxygen by N, C or S into a large band gap metal oxide catalyst anionic network (anionic doping). Hara et al, 2004 showed that Ti-O-N system band gap energy could be tuned by adjusting the amount of doped nitrogen and thereby, the electrical properties of the material can be modified. Recently in a brief report (Priya and Kanmani, 2009 and 2011) we have demonstrated the synthesis of CdS-ZnS where the coprecipitation method was used to produce the complex catalyst.

This paper presents the work on the elaborate synthesis of nanosize ZnO-TiO₂ photocatalyst with the extensive characterization by Scanning Electron Microscope (SEM), X-Ray Diffractometer (XRD), Ultraviolet Visible Diffuse Reflectance Spectroscopy (UV-DRS), Fourier transform Infrared Spectroscopy (FTIR). The interesting outcome of this study is that the synthesized ZnO-TiO₂ is found to be an excellent photocatalyst and it is more active than other catalysts under visible light irradiation for the production of hydrogen from sulfide wastewater.

2. MATERIALS AND METHODS

Method of preparing the ZnO-TiO₂ powders was similar to that mentioned in the literature (Liu et al., 2004, Fan et al., 2006) using sol-gel method. Appropriate cerium nitrate (Zn(NO₃)₂.6H₂O, HIMEDIA, U.S.A) was dissolved in distilled water in the ratio of 1:8 and the pH of the mixture solution was adjusted to 1.5 using Nitric acid (HNO₃, MERCK, U.S.A), then titanium Isopropoxide solution (C₃H₇Ti, SPECTROCHEM, India) was added drop by drop to the mixed solution with constant stirring for 10-12 hours. The white precipitate was formed instantaneously. The resulting colloid solution was concentrated at 35-40°C in a rotary evaporator. The final solution with the precipitate was filtered and dried and given heat treatment at 400°C for 2 hours using muffle furnace.

The phase identification of the powder was conducted at room temperature using X-Ray Diffractometer (XRD, CuKα1, λ= 1.54 nm, PANalytical, Netherlands). The phase and particle size were determined using Scherrer equation. Scanning Electron Microscopy (SEM, S3400N, HITACHI, Japan) was used to analyze the particles morphology and the agglomeration.

UltraViolet – Visible Spectroscopy (UV-DRS) was used to find out the threshold wavelength and bandgap was determined by Getoff and Linselbierger equation and Fourier Transform Infrared Spectroscopy (FT-IR, PERKIN ELMER, U.S.A) which was used to confirm the doping and the surface adsorption of the prepared photocatalyst.

The PCD experiments were conducted using a batch type (Acrylic) reactor holding 500 mL of the respective synthetic wastewater sample batch with ZnO-TiO₂. Fig 1 provides the reactor details. Batches of synthetic wastewater samples were prepared using distilled water and stock solution was prepared from...
using Sodium sulfide (MERCK, U.S.A) and Sodium sulfite (MERCK, U.S.A). For the PCD experiments, effects of various parameters like sulfite concentration, pH of the wastewater, dosage of the catalyst, Volume of the wastewater and finally its performance were compared using various catalysts. The synthetic wastewater batch with ZnO-TiO$_2$ was transferred to PCD reactor. A 150 W near visible lamp (PHILIPS) that emits rays at a wavelength 615-700 nm with the peak maximum at ~ 682 nm was then positioned at the centre of the reactor. The light source and reactor are separated at least with a distance of 15 cm. The visible lamp was turned on during the course of the study. The reaction was carried out from 0 to 30 minutes, after which the samples were collected. The hydrogen produced is collected through downward displacement of water. The hydrogen production from sulfide conversion was calculated using the below mentioned formula.

\[
\text{Sulfide conversion (Y) in } \% = \frac{\text{Moles of } H_2 \text{ produced}}{\text{Moles of } Na_2S \text{ fed}} \times 100
\]

The moles of $H_2$ produced in the reaction have been calculated using Ideal gas equation. The alkaline solution (NaOH, MERCK) was used in order to fix the gas errors. The hydrogen collected in the downward displacement was tested using Gas chromatograph (GC 2014, SHIMADZU, Japan) which was equipped along with the conductivity detector for hydrogen. The Gas chromatograph was calibrated regularly using known concentration of hydrogen. The pH analyses were completed using a pH meter setup (ELICO, India)

3. CHARACTERIZATION OF PHOTOCATALYST

3.1 SEM

The ZnO-TiO$_2$ powder prepared by sol-gel process method was crystalline with a slight yellow colour. The SEM micrograph of ZnO-TiO$_2$ is shown in Fig.2 which indicates that the agglomeration of particles was observed which was due to the result of doping (Liu et al., 2005).

Fig. 2. SEM micrograph of ZnO-TiO$_2$

3.2 XRD

The XRD pattern of ZnO-TiO$_2$ is shown in Figure. 3. indexed using ISCD no. 86-1157. The indexing study indicates that the powder consists of tetragonal ZnO -TiO$_2$ in a body centered cubic lattice configuration with a particle size of 32.4 nm which was determined with the strong peak (101) at $2Theta$ = 25.5$^\circ$ of the ZnO-TiO$_2$ phase. The particle size is smaller than pure TiO$_2$ which was due to doping of cerium which can cause the change in quantum size effect (Hoffmann et al., 1995). The pattern also reveals that anatase peaks are more dominant than rutile. The inhibition of phase transition was ascribed to the stabilization of anatase phase by the Ce through the formation of Ti-O-Zn bonds (Zhang et al., 1998). The stability of the anatase peak was due to the electron density imparted by the cerium to TiO$_2$ (Ranjit et al., 1997).

Fig. 3. XRD of ZnO-TiO$_2$
3.3 UV-DRS

The UV-DRS pattern of Figure. 4. was indexed with the UV-DRS spectrum of Gao et al., 2000. The pattern discloses the fact that, after doping, there was a change in band gap and in threshold wavelength. The band gap energy changed from 3.2 eV to 1.7 eV. This modification was due to the dispersion of ceria component in the TiO$_2$ (Coronado et al., 2002).

![Fig 4 UV_DRS of ZnO-TiO$_2$](image)

4. RESULTS AND DISCUSSION

Photocatalytic studies for the production of simulated sulfide wastewater were conducted in earlier experiments. First the experiments were conducted at optimizing the sulfite concentration because the sulfite concentration plays a significant role in erratic behaviour of sulfide nature. Three concentrations which were taken for the study are 0.15, 0.25 and 0.35 M. among that; the greater production of hydrogen production and sulfide conversion of maximum was attained at the concentration of 0.25 M. Table. 1 shows the hydrogen production and sulfide conversion with respect to change in sulfite concentration.

<table>
<thead>
<tr>
<th>Sulfite Concentration in Moles</th>
<th>H$_2$ Production in µmol h$^{-1}$</th>
<th>Sulfide conversion in mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>3068</td>
<td>204</td>
</tr>
<tr>
<td>0.25</td>
<td>5189</td>
<td>207</td>
</tr>
<tr>
<td>0.35</td>
<td>2231</td>
<td>63</td>
</tr>
</tbody>
</table>

Table. 1. Effect of Sulfite Concentration

All of these experiments are carried out for 30 minutes of irradiation. The adsorption was maximum at 0.25 M so it attained the higher photocatalytic activity. Also, at some concentrations the wastewater occupies more active sites than the OH$^-$ radicals which causes the low photocatalytic activity (Kashif and Ouyang, 2009).

Following the sulfite optimization, pH optimization should be performed because of its prominent role in existing nature of the sulfur compounds. The three basic pH 11, 12 and 13 were tried to find the favourable pH for the maximum hydrogen production and sulfide conversion. Table 2 shows the hydrogen production and sulfide conversion with respect to change in pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>H$_2$ Production in µmol h$^{-1}$</th>
<th>Sulfide conversion in mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>1394</td>
<td>57</td>
</tr>
<tr>
<td>12</td>
<td>5245</td>
<td>209</td>
</tr>
<tr>
<td>13</td>
<td>2510</td>
<td>100</td>
</tr>
</tbody>
</table>

Table. 2. Effect of pH

pH 12 which is a natural pH of the simulated wastewater was found to have the maximum hydrogen production and sulfide conversion at 30 minutes of irradiation. In photocatalytic treatment of sulfide or thiosulfate wastewater, the natural pH was found to be in favour of the photocatalytic activity (Vohra et al., 2011). The basic pH imparts the hydroxyl group to the surface which causes the increase in adsorption of pollutant to TiO$_2$ surfaces. The hydroxyl groups when it integrates to the active sites provides a higher photocatalytic activity (Jiangrong et al, 2006). At a low pH, the surface charges of ZnO and TiO$_2$ would be positive, and at high pH, both particles won’t have much effective contact and charge transfer from Zn and TiO$_2$ (Hoffmann et al, 1995). In order to use the catalyst in efficient manner, effect of dosage was done to know the amount of catalyst needed for efficient
After optimizing all the parameters in the treatability studies, the performance of the ZnO - TiO₂ was compared with the existing catalysts, Nano TiO₂ and Degussa TiO₂. The hydrogen production and sulfide conversion in the study were given in the table. 5.

<table>
<thead>
<tr>
<th>Table 3. Effect of Catalyst dosage</th>
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<tr>
<td>Catalyst dosage in g</td>
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<tr>
<td>-----------------------</td>
</tr>
<tr>
<td>0.05</td>
</tr>
<tr>
<td>0.1</td>
</tr>
<tr>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 3 provides data regarding the hydrogen production and sulfide conversion in table with respect to change in dosage of the catalyst. The greater photocatalytic activity was achieved at 0.1 g proving it as the optimum catalyst dosage, as a large surface area is available for adsorption of dye followed by its degradation. Above the optimum value, the solution opacity increases which affects the light penetration through the solution leading to a decrease in rate of degradation. After optimizing dosage, the volume of the wastewater was taken for the study. Varying amounts of wastewater 100, 300, 500 mL were taken for the study. The hydrogen production and sulfide conversion are presented in table 4.

<table>
<thead>
<tr>
<th>Table 4. Effect of Volume</th>
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<tbody>
<tr>
<td>Volume in mL</td>
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<tr>
<td>--------------</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>200</td>
</tr>
<tr>
<td>500</td>
</tr>
</tbody>
</table>

The high activity of the ZnO - TiO₂ is due to the electron density imparted to the TiO₂ surface by the cerium. Li et al (2006a) works also gives the required evidence that using of Cerium with TiO increases the hydrogen production. The photocatalytic activity is Zn-TiO₂ is also stable because of the stabilization of anatase phase by the surrounding earth oxides throughout the formation of Ti-O-Zn element bonds (Zhang et al, 2008) which causes the change in amount of hydroxyl groups resulting from the interaction between the Cerium and TiO₂ (Lin et al, 1999).

5. CONCLUSION

The Tetragonal, body centered cubic crystal structure like ZnO-TiO₂ in the anatase phase was efficiently synthesized with sol-gel method. The powders possess small band gap energy with threshold wavelength in the visible region. The photocatalyst was optimized through treatability studies. 0.1 g of catalyst dispersed in 500 mL of simulated sulfide wastewater (10000 mg/L) irradiated under the visible lamp of 150 W produced the hydrogen of 5189 µmol h⁻¹ with the sulfide conversion of 2.07 % (207.5 mg/L). The
performance of ZnO-TiO₂ was found to be best than Nano TiO₂ and Degussa TiO₂.

REFERENCES


composite tubular ultrafiltration (UF) membranes', Desalination, Vol. 196, pp. 76-83.


