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PHOTOCATALYTIC HYDROGEN GENERATION BY ETHANOL ASSISTED WATER SPLITTING REACTION USING MIXED OXIDE OF Ba AND Mn

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Abstract- Visible light active $BaMnO_x$ type photocatalyst was synthesized by using sol-gel method. The photocatalyst was characterized by X- ray diffraction, BET-SA, and UV-visible diffused reflectance spectroscopy (UV-DRS). $BaMnO_x$ photocatalyst exhibited an optical band gap of 2.9 eV with the absorption predominantly in visible region of the light spectrum. The crystallite size of $BaMnO_x$ is 24.63 nm as calculated by the Debye Scherer equation. The BET surface area value for $BaMnO_x$ photocatalyst was found to be 16.2 m^2/g. The photocatalytic hydrogen generation was carried out by using Pt as co-catalyst and ethanol as a sacrificial donor. Hydrogen generation was investigated by ethanol assisted water splitting reaction under visible light irradiation, using a compact glass reactor and tungsten lamp as a source of visible light. The rate of photocatalytic hydrogen evolution was observed to be 7463 $\mu mol.g^{-1}.h^{-1}$ of Pt-$BaMnO_x$ photocatalyst.
Keywords- Photocatalysis, visible light activity, hydrogen generation, perovskite, $BaMnO_x$.

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Introduction

Hydrogen has been projected as one of the renewable sources of energy and future alternative for the conventional fuel [1]. The issues like limitations of the reserves of the fossil fuel and their environmental damages are the main drivers for the hydrogen based energy in future [2]. Generation of hydrogen from renewable sources like water and utilizing the solar radiations is the most attractive and potential option as per the following reaction [3]:

H_2O à H_2 + ½ O_2, ΔG=+238 KJ/mol --- (1)

As observed from equation 1, water can be split into H_2 and ½ O_2, and the dissociation of water can occurs at 1.23 eV, which otherwise requires a very high temperature [4, 5,]. To overcome these problems, the photocatalytic way of hydrogen generation from water can be an alternative and cleaner route, despite many practical challenges.

Titanium dioxide was the first material used for electrochemical water splitting reaction by Fujishima and Honda in 1972 under ultra-violet radiations [6]. Extensive attempts were made by different researchers to design visible light active photocatalysts, to utilize the maximum amount of solar energy [7]. Various photocatalysts like metal oxides, perovskites, layered perovskites, mixed metal oxides etc have been widely developed, studied and used for the generation of hydrogen [8-12]. Perovskite/ mixed metal oxides type materials are stable, crystalline and very flexible in their composition and can incorporate various metal ions in their structure [13]. As photocatalytic water splitting reaction is a redox reaction and the mixed metal oxide type compounds exhibit both reducing as well as oxidizing properties, several perovskite and mixed oxides type materials have been reported for the photocatalytic hydrogen generation reaction [9-12].

Material and Methods:

Materials

Barium nitrate, manganese nitrate and citric acid were used for the synthesis of mixed oxide type $BaMnO_x$ without further purifications.

Synthesis

Mixed oxide $BaMnO_x$ was synthesized by sol gel method. Barium

nitrate was used for Ba as A-site element and Mn for B-site element. DI water was used to prepare aqueous solutions. The respective salt solutions were mixed and homogenized by constant stirring. The formation of gel was observed. It was then kept for drying in an oven at 90^0C and then pre-calcined at 500^0C for 2 h to remove all the organic impurities present in the mixture. It was then finely ground in a mortar- pestle and re- calcined in air at 700^0C for 4h.

Characterization

The photocatalyst was characterized by XRD and UV-DRS techniques. The crystallite size and crystalline phase of photocatalyst $BaMnO_x$ was studied by X- ray diffraction (XRD) using Rigaku Miniflex II Desktop X-ray diffractometer with Cu Kα radiation source at 30kV and 15mA and using a scanning rate of 5^0/ min.
The BET surface area analysis was performed by using Quantachrome Autosorb-1, in thermo stated bath at liquid nitrogen temperature of 77^0K. The UV-Vis diffuse reflectance spectrum (UV -DRS) was obtained by using Spectophotometer UV-1800 UVDRS Shimadzu, while $BaSO_4$ was used as a reference material.

Photocatalytic evaluation

The photocatalytic experiments have been carried out in a close type photocatalytic glass reactor. 10 ml of DI water was boiled to remove dissolved oxygen. It was then cooled and to it optimized dose of photocatalyst $BaMO_x$ was added followed by addition of known quantity of ethanol, and co-catalyst platinum. The whole experimental set-up was evacuated by using vacuum pump to remove air from the system. The solution was continuously stirred using magnetic stirrer for uniform dispersion of the photocatalyst. The glass reactor was illuminated with two 200W tungsten light sources for 4 hours. After the completion of reaction, the generated hydrogen was evaluated on the GC equipped with molecular sieve 5A column using thermal conductivity detector (TCD)

Results and discussion

Highly crystalline structure of $BaMnO_x$ was confirmed by the XRD pattern as shown in Fig.1, however, it was found to be a mixture of a few crystalline phase instead of a single phase. The crystallite size of $BaMnO_x$ has been determined by using the Debye-Scherer formula.

$$D = K.\lambda / \beta.\cos\theta$$

Where, 'D' is the crystallite size of particle (A^0), 'K' crystallite shape factor, 'λ' is X-ray wavelength (1.5418 A^0 for Cu Kά), β is the width of diffraction peak, and θ is the observed peak angle (degree). The observed crystallite size value for $BaMnO_x$ photocatalyst is 24.63 nm considering the high intensity peak.

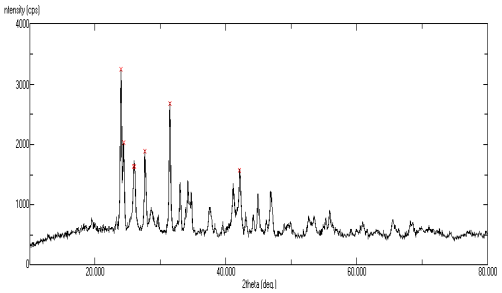

Fig. 1- XRD of $BaMnO_x$ photocatalyst

The optical characterization of photocatalyst was performed by UV - DRS as shown in Fig.2. The UVDRS spectrum for $BaMnO_x$ semiconductor indicates the absorbance of light nearly at 428 nm. The band gap energy of $BaMnO_x$ photocatalyst is therefore estimated to be 2.9 eV as calculated by using the formula, (Band gap=1240/ λ) [14]. This shows that the synthesized $BaMnO_x$ photocatalyst is a visible light active compound.

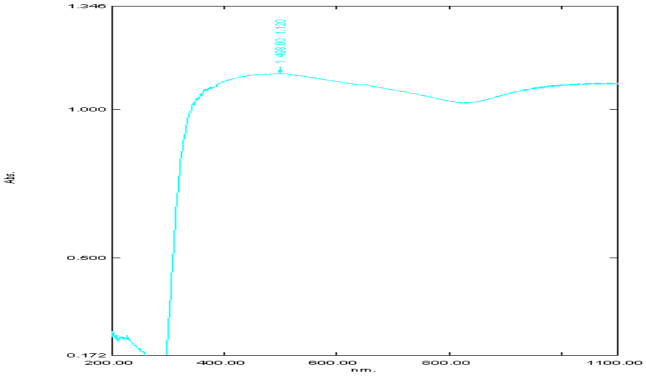

Fig. 2- UV-DRS of $BaMnO_x$ photocatalyst

Photocatalytic activity

The synthesized photocatalyst has been evaluated for their activity towards hydrogen generation through ethanol assisted splitting of water under visible light radiations, by using Pt as a co-catalyst. The photocatalyst $BaMnO_x$ shows a hydrogen yield of 7463 $\mu mole.g^{-1}.h^{-1}$. This is substantial considering the mixed oxide phase.

Mechanistic Aspects

Based on the above discussed results and related literature, the mechanistic aspects for photocatalytic activity of ABO_x type $BaMnO_x$ photocatalyst for the water splitting reaction under visible light are proposed. Photocatalyst $BaMnO_x$ absorbs the photons of visible light with energy greater than the band gap, leading to photoexcitation of electron from valence band to conduction band. The electron excitation from VB leaves the hole and simultaneous redox reaction usually takes place on Pt site. The electron at CB and hole at VB facilitate the oxidation and reduction of water molecule to finally generate O_2 and H_2. Sacrificial donor like ethanol donates electron to prevent recombination reaction and the chain of photoexcitation reaction thus continues. The co-catalyst platinum is expected to provide sites to atomic hydrogen with the transfer of electron from CB to produce hydrogen molecule. For overall water splitting reaction in the visible region of solar spectrum, it should have band gap energy roughly in between 1.23 to 3eV. The synthesized $BaMnO_x$ photocatalyst shows a band gap energy of 2.9 eV as confirmed by UVDRS studies. This also infers the visible light activity of compound. In this way, the mixed oxide type $BaMnO_x$ appears to follow a mechanism of photocatalytic water splitting, quite typical for semiconductor metal oxide.

Conclusion

The $BaMnO_x$ photocatalyst was synthesized by using sol-gel method. The XRD pattesrn of synthesized $BaMnO_x$ shows crystallite size of 24.63 nm and suggest a mixure of phases. The UV-DRS shows a visible light active compound with optical band gap of 2.9

eV. The photocatalytic activity of $BaMnO_x$ sample was evaluated by photocatalytic water splitting reaction with the hydrogen generation of 7463 µmole.g^{-1}.h^{-1}. This is a reasonably good hydrogen generation in visible light illumination and also considering the surface area 16.2 m^2/g of $BaMnO_x$ photocatalyst. Thus photocatalytic approach for hydrogen generation shows as a potential alternative path of cleaner energy production for future. Further modifications of materials including various synthesis procedures, preparation of supported and doped metal oxides are in progress to attempt further improvement in photocatalytic properties.

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References

[1] Ni M., Leung M.K.H., Leung D.Y.C., Sumathy K. (2007) *Renewable and Sustainable Energy Reviews*, 11, 401- 425A.

[2] Kudo and Miseki Y. (2009) *Chem. Soc. Rev,* 38, 253-278.

[3] Navarro R.M., Sanchez-Sanchez M.C., Alvarez-Galvan M.C. del Valle F. and Fierro J.L.G. (2009) *Energy Environ. Science*, 2, 35-54.

[4] FAN Y., LI D., DENG M., LUO Y. and MENG Q. (2009) *Front. Chem,* 4(4), 343-351.

[5] Oudenhoven J.F.M., Scheijen F.J.E. and Wolffs M. (2004) *Chemistry of catalytic system 2, photocatalysis,* 1-22.

[6] Fujishima A. and Honda K. (1972) *Nature*, 283 37.

[7] Li F., Liu Y., Liu R., Sun Z., Zhao D., Kou C. (2010) *Materials Letters*, 64 223-225

[8] Choi J., Ryu S., Balcerski W. Lee T.K. and Hoffmann M.R. (2008) *Journal of Materials Chemistry*, 18, 2371-2378.

[9] Yang Liua C., Lei Xiea (2008) *Journal of Power Sources*, 183, 701-707.

[10] Kudo A. (2005) *international journal of hydrogen energy*.

[11] Jae Sung Lee (2005) *Catalysis Surveys from Asia*, 9(4).

[12] Kanade K.G., Baeg J.O., kong K.J., Kale B.B., lee S.M., Moon S.J., lee C., yoon S. (2008) *International journal of hydrogen energy*, 33, 6904-6912.

[13] Tanaka H., Misono M. (2001) *Current option in solid state and material sciences*, 5, 381-387.

[14] Joshi M.M., Labhsetwar N.K., Manglurkar P.A., Tijare S.N., Kamble S.P., Rayalu S.S. (2009) *Applied catalysis A: General*, 357 26-33