Photocatalytic hydrogen generation with Ag-loaded LiNbO₃

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Abstract. In this contribution LiNbO₃ and Ag-loaded LiNbO₃ photocatalysts were tested in the reaction of hydrogen evolution. The silver modified samples contained different loading of co-catalyst in the range of 0.5–4 wt%. It was essential to optimize the sample composition to achieve an efficient hydrogen evolution. The optimal sample contained 2 wt% of silver. The detailed analysis indicated that silver was deposited on the surface of LiNbO₃ in the form of Ag₂O. Therefore, it is supposed that Ag₂O was responsible for the enhanced photocatalytic activity in the studied reaction. The crystallographic phases and optical and vibronic properties were examined by X-ray diffraction (XRD) and diffuse reflectance (DR) UV–Vis and resonance Raman spectroscopic methods, respectively. Morphology of the produced samples were studied using a high-resolution transmission electron microscope (HRTEM).

Keywords. Lithium niobate; Ag₂O; photocatalysts; hydrogen evolution.

1. Introduction

Lithium niobate (LiNbO₃) is one of the most excellent functional materials due to its outstanding physical properties such as piezoelectrical, electrooptical, pyroelectrical and photorefractive properties. It has useful applications for surface acoustic wave devices, waveguides in integrated optics, infracted sensors, etc (An *et al* 2002; Simoes *et al* 2003; Liu and Xue 2006; Hao *et al* 2009; Chen *et al* 2012). On the other hand, it fully fills all requirements (such as flat band potential and the number of photons absorbed) of a good potential as a photocatalyst for hydrogen generation. However, there are only few reports investigating the photocatalytic properties of LiNbO₃ (Chen *et al* 2004; Saito *et al* 2011; Stock and Dunn 2012). Chen *et al* (2004) reported that LiNbO₃ synthesized via solid-state reaction was active in the reaction of photocatalytic hydrogen generation in the presence of methanol. Saito *et al* (2011) stated that LiNbO₃ nanowires produced by a metal complex-based method showed good photocatalytic activity for water splitting. Moreover, they found that LiNbO₃ nanowires showed enhanced photocatalytic properties as compared with LiNbO₃ prepared by a solid-state reaction. Additionally, the activity of LiNbO₃ and Fe- and Mg-doped LiNbO₃ in the reaction of photocatalytic acid black 1 and rhodamine B decomposition under solar illumination was also reported (Stock and Dunn 2012). In this study, the authors point out that LiNbO₃ is an active photocatalyst for organic dyes decomposition under solar irradiation

and Mg-doped LiNbO₃ exhibits higher photocatalytic activity than pure LiNbO₃. In our previous work (Zielińska *et al* 2008), several chemical compounds based lithium niobate prepared via impregnation followed by calcination were tested in the reaction of photocatalytic hydrogen generation. The results indicated that the most active catalyst for the photocatalytic generation of hydrogen is the one containing two lithium niobate phases: LiNbO₃ and LiNb₃O₈.

It is known that loading co-catalysts on the surface of photocatalysts is often essential for achieving efficient hydrogen evolution. The loaded co-catalysts can capture the photogenerated electrons reducing the electron–hole recombination and act as reaction sites for proton reduction (Kudo 2006; Chen *et al* 2010; Puangpetch *et al* 2010; Yu *et al* 2011). For example, Yu *et al* (2011) stated that CuO is effective co-catalyst for TiO₂ to enhance the photocatalytic hydrogen production. The amount of hydrogen obtained in the presence of 1.3 wt% CuO/TiO₂ was about 129 times greater than that in the presence of pure TiO₂. Kudo (2006) studied photodecomposition of water in the presence of many different tantalate photocatalysts. The author indicated that loading with NiO co-catalyst, which works as H₂ evolution site, drastically improves the photocatalytic activity of tantalates. The activity of SrTiO₃ with different loaded metal co-catalysts (Au, Pt, Ag, Ni, Ce and Fe) in the reaction of photocatalytic hydrogen production from a methanol aqueous solution was studied (Puangpetch *et al* 2010). Here, the authors stated that Au, Pt, Ag and Ni loadings have a positive effect on the photocatalytic activity of SrTiO₃ under both UV and Vis light irradiation.

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In the present study, the synthesis, characterization and photocatalytic properties of unmodified LiNbO_3 and Ag-loaded LiNbO_3 for the reaction of photocatalytic hydrogen generation will be presented. The influence of silver content on the photocatalytic activity of Ag/ LiNbO_3 materials for photocatalytic hydrogen generation has been investigated. The photocatalytic reactions were carried out in the presence of formic acid.

2. Experimental

2.1 Preparation of LiNbO_3 and Ag-loaded LiNbO_3 photocatalysts

All the initial reagents, Nb_2O_5 , $\text{LiOH}\cdot\text{H}_2\text{O}$ and AgNO_3 were used as received without further purification (Sigma-Aldrich). In a typical synthesis, first Nb_2O_5 was dissolved in an aqueous solution of lithium hydroxide with vigorous stirring. The molar ratio of $\text{LiOH}:\text{Nb}_2\text{O}_5$ was 2:1, respectively. After the addition of Nb_2O_5 , the mixture was continually stirred for 3 h above the boiling temperature. The solid material was dried at the temperature of 70 °C and grounded in a mortar until the fine powder was obtained. Next, the sample was calcined in the temperature of 550 °C in air for a controlled time between 5 to 20 h with step of 5 h. Finally, the excess of LiOH was washed out with water.

Silver was loaded as a co-catalyst on the produced LiNbO_3 by conventional impregnation/calcination procedure. Typically, LiNbO_3 powder was introduced to the aqueous solution of silver nitrate and stirred vigorously until the homogeneous suspension was observed. During the experimental procedure the samples with Ag loading in the range of 0.5–4 wt% were prepared. Water was evaporated during the slow heating and constant stirring. The resulting products were dried at 70 °C for 24 h and then calcined at 400 °C for 4 h.

2.2 Photocatalysts characterization

The crystallographic structures of the prepared samples were confirmed by X-ray diffraction analysis (X'Pert PRO Philips diffractometer, $\text{CoK}\alpha$ radiation). UV-Vis diffuse reflectance spectra were recorded using a UV-Vis spectrometer (Jasco, Japan). Raman measurements were performed using a Resonance Raman Renishaw In Via Microscope spectrometer with a laser length of 785 nm. The morphology of the photocatalysts was investigated by high-resolution transmission electron microscopy (HR-TEM-*FEI Tecnai F30*).

2.3 Photocatalytic reactions

The photocatalytic reactions were carried out at room temperature under atmospheric pressure in a closed

system with an inner irradiation-type photoreactor using a Hg lamp (150 W). The rate of H_2 evolution was determined in an aqueous solution of 0.1 M formic acid

Figure 1. XRD patterns of Nb_2O_5 (a) and material produced after calcination of Nb_2O_5 and LiOH at temperature of 550 °C for 5, 10, 15 and 20 h (b–e).

Figure 2. XRD patterns of LiNbO_3 (a) and Ag-loaded LiNbO_3 with 0.5 (b), 1 (c), 2 (d), 3 (e) and 4 (f) wt% of Ag.

Figure 3. TEM images of unmodified LiNbO₃ (a) and Ag-loaded LiNbO₃ with 0.5 (b), 2 (c) and 4 (d) wt% of Ag.

(700 mL) containing 200 mg of the catalyst. Before light irradiation, nitrogen was bubbled through the reaction mixture for 60 min to remove dissolved oxygen to ensure that the reaction system is under anaerobic condition. Finally, the solution was irradiated for 150 min without argon purging. The evolved hydrogen was collected and analysed by a gas chromatography (Chrome 5) equipped with a thermal conductivity detector (TCD).

3. Results and discussion

3.1 Characteristics of produced catalysts

The crystallographic composition of all investigated samples was studied via XRD. Figure 1 shows XRD patterns of Nb₂O₅ original (pattern a) and the materials produced after calcination of Nb₂O₅ and LiOH at a temperature of 550 °C for different periods (5, 10, 15 and 20 h – patterns b–e). Figure 1 exhibits that the samples obtained for 5, 10

and 15 h are composed of a mixture of lithium niobate with a rhombohedral structure (LiNbO₃, JCPDS card no. 85-2456) and niobium oxide (Nb₂O₅). However, the relative intensity of the corresponding peaks is altered. When the annealing time increases to 20 h, all the diffraction peaks can be indexed to LiNbO₃ and no diffraction peaks from unreacted Nb₂O₅ are presented. XRD patterns of unmodified LiNbO₃ and Ag-loaded LiNbO₃ samples are presented in figure 2. The detailed phase analysis reveals that Ag/LiNbO₃ photocatalysts contain additional phase of Ag₂O (JCPDS card no. 03-0796).

The morphology of the samples was studied using HR-TEM. Here, only pristine LiNbO₃ and three representative Ag-loaded samples with 0.5, 2 and 4 wt% of Ag will be presented. TEM images for the above mentioned samples are shown in figure 3. TEM analysis reveals high crystallinity in all the investigated samples. Moreover, it can be seen that in Ag/LiNbO₃ samples (images b–d), new phase is dispersed. The new phase can be attributed

Figure 4. Raman spectra of samples: LiNbO_3 (a) and Ag-loaded LiNbO_3 with 0.5 (b), 1 (c), 2 (d), 3 (e) and 4 (f) wt% of Ag.

Figure 5. Diffuse reflectance UV-Vis absorption spectra (A) and Kubelka-Munk plot for bandgap evaluation (B) of Nb_2O_5 (a) and LiNbO_3 (b).

to Ag_2O and is composed of the nanoparticles in the range of 2–5 nm. These results are consistent with XRD measurements.

Next, the samples were investigated by means of Raman spectroscopy. Figure 4(A) shows Raman spectra of the unmodified LiNbO_3 (spectrum a) and Ag-loaded LiNbO_3 samples (spectra b–f) in the region between 100 and 1000 cm^{-1} . The clear Raman bands at 151, 237, 257, 275, 319, 368, 430, 580, 626 and 874 cm^{-1} can be observed for LiNbO_3 . In the spectra of Ag/ LiNbO_3 all

bands characteristic for LiNbO_3 have also been observed. Moreover, in figure 4(A), a new broad band in the region of 730–850 cm^{-1} ($\sim 790 \text{ cm}^{-1}$) is detected for Ag/ LiNbO_3 samples. Raman spectra of all investigated samples in the range of 1000 and 1800 cm^{-1} are shown in figure 4(B). No Raman modes in the region of 1000 and 1800 cm^{-1} have been detected for LiNbO_3 . Here, one can notice that in Ag/ LiNbO_3 spectra new Raman modes at about 1060 cm^{-1} and a split broad band in the region of 1437–1690 cm^{-1} are observed. All those peaks are characteristic

for Ag₂O. Raman spectrum of Ag₂O exhibited five bands at 251, 722, 1042, 1465 and 1959 cm⁻¹ (Mohammed *et al* 2012). The peaks at 251 and 1042 cm⁻¹ in Raman spectrum of Ag₂O are related to the stretching (Ag–O) mode between Ag and O atoms. Here, clear agreement with XRD data is demonstrated.

DR–UV–Vis absorption spectra were measured in order to characterize optical properties of Nb₂O₅, LiNbO₃ and Ag/LiNbO₃ samples. To determine the bandgap energy of the investigated samples, the Kubelka–Munk method based on DR–UV–Vis spectra was employed. Greater details of the bandgap energy estimations have

been provided in the literature (Zielińska *et al* 2011). Figure 5 shows DR–UV–Vis spectra of the pristine Nb₂O₅ (spectrum a) and produced LiNbO₃ (spectrum b). This figure presents two plots: A and B. Figure 5(A) shows absorption spectra while figure 5(B) illustrates the plot of $(F(R)h\nu)^{1/2}$ vs photon energy ($h\nu$) for Nb₂O₅ and LiNbO₃. As shown in this figure, a single absorption edge can be clearly observed for Nb₂O₅ and LiNbO₃. Moreover, the absorption edge of LiNbO₃ is shifted towards the shorter wavelength in respect to Nb₂O₅. It indicates that the blue shift of the bandgap energy occurred. The estimated bandgap energy of Nb₂O₅ and LiNbO₃ samples are 3.07 and 3.86 eV. The estimated value of bandgap of produced LiNbO₃ is similar to that described in the literature (Hao *et al* 2011; Tiwari and Dunn 2012). DR–UV–Vis spectra of Ag/LiNbO₃ samples are presented in figure 6. Here one can notice that all Ag/LiNbO₃ samples have strong absorption in the visible light region with respect to the starting LiNbO₃. This is characteristic for Ag₂O (Wang *et al* 2011). The reported values of the bandgap of Ag₂O based on optical absorption edge ranges from 0.49 to 3.1 eV (Fang *et al* 2011). This is in full agreement with XRD and Raman data of the presented samples.

Figure 6. UV–Vis spectra of samples: LiNbO₃ (a) and Ag-loaded LiNbO₃ with 0.5 (b), 1 (c), 2 (d), 3 (e) and 4 (f) wt% of Ag.

Figure 7. Photocatalytic H₂ evolution over LiNbO₃ and Ag-loaded LiNbO₃ catalysts (HCOOH concentration – 0.1 mol/L/dm³, amount of catalysts – 0.2 g).

3.2 Photocatalytic reactions

The photocatalytic hydrogen production studies were conducted over unmodified LiNbO₃ and silver modified LiNbO₃ catalysts in formic acid–water mixture under UV light irradiation. The comparison of hydrogen evolution over LiNbO₃ and Ag/LiNbO₃ photocatalysts is presented in figure 7. It can be seen that silver loading improved the photocatalytic activity of LiNbO₃. The explanation of higher photocatalytic activity of Ag-loaded LiNbO₃ than that of unmodified LiNbO₃ can be explained by the higher electronegativity of Ag (1.93) as compared to that of Nb (1.60), resulting in easier photoexcited electron transfer from LiNbO₃ conduction band to the Ag species. This efficient electron transfer can inhibit rapid recombination of electron–hole pairs, leading to higher activity of Ag/LiNbO₃ composites for photocatalytic hydrogen production. Moreover, it is possible that for Ag-loaded LiNbO₃ catalysts silver species works as active sites for proton reduction (Puangpetch *et al* 2010; Onsuratoom *et al* 2011). Based on the obtained results a possible mechanism of photocatalytic hydrogen generation from aqueous solution of formic acid and over Ag/LiNbO₃ is proposed below (1–6) (Zheng *et al* 2009; Zheng *et al* 2010):

Figure 8. Effect of Ag content in catalysts on H₂ evolution rate.

In the initial stage (1), light is absorbed by photocatalysts to produce electron–hole pairs. The molecules of water in the formic acid solution split into hydroxyl radicals ($\cdot\text{OH}$) and H^+ ions through H_2O oxidation (2). The hydroxyl radicals thus obtained generate molecular water and oxygen (3). In the next step (4–5), HCOOH dissociates to HCOO^- and H^+ ions. The photogenerated holes attack the produced HCOO^- to form H^+ and CO_2 . H^+ ions produced during whole process (2 and 4) transfer to the loaded-Ag species, where reduction to H_2 by photogenerated electrons occurred (6).

The presented results clearly indicate that the kinetics of hydrogen generation during the first 150 min of irradiation can be described by zero-order kinetics. The effect of Ag content in catalysts on H₂ evolution rate is presented in figure 8. Here, the amount of released hydrogen increases when the content of Ag increases from 0.5 to 2 wt%. As the amount of loaded silver was > 2 wt%, the activity of modified materials were decreased. The amount of the generated hydrogen increased from 1.57 $\mu\text{mol/min}$ (0.5 wt%–Ag/LiNbO₃) to 2.28 $\mu\text{mol/min}$ (2 wt%–Ag/LiNbO₃) and then decreased to 1.53 $\mu\text{mol/min}$ (4 wt%–Ag/LiNbO₃). This effect can be explained by the partial blockage of LiNbO₃ surface active sites due to excessive amount of silver species (Hao *et al* 2011). Moreover, it is possible that at high Ag content, Ag₂O would tend to aggregate into larger particles which results in a negative impact on Ag/LiNbO₃ composite activity (Long *et al* 2006; Hao *et al* 2011; Tran *et al* 2012).

4. Conclusions

The synthesis and detailed characterization of unmodified LiNbO₃ and Ag-loaded LiNbO₃ photocatalysts were described. Moreover, the activities in the reaction of photocatalytic hydrogen evolution in the presence of formic acid of unmodified LiNbO₃ and Ag-loaded LiNbO₃ samples have been shown. The following conclusions are provided: (i) pure LiNbO₃ was synthesized after calcination of Nb₂O₅ and LiOH at the temperature of 550 °C for 20 h, (ii) Ag₂O oxides on Ag/LiNbO₃ was confirmed, (iii) a significant enhancement of the photocatalytic efficiency of Ag-loaded LiNbO₃ as compared to unmodified LiNbO₃ was observed and (iv) the highest H₂ evolution efficiency was observed for Ag/LiNbO₃ photocatalyst with 2 wt% silver content.

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