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Mesoporous SnO_x/TiO₂ Materials as Photocatalyst for Water Splitting Reaction

M. Stodolny, A. Mikołajczak, M. Łaniecki, A. Mickiewicz University, Poland

1 Introduction

Transformation of solar energy towards other storable form of energies is a big challenge both for science and academia. There are two ways of solar energy transformations: direct and indirect. In the first one, solar energy in photocells is directly transformed into electric energy. The main disadvantage of wider application is related with low energy density accumulated this way. An alternative energy carrier can be based on hydrogen. This energy carrier seems to be ideal from environmental reasons because the only “ash” is represented by water. Moreover, hydrogen is easy in storage and transport. It can be produced from water either by photocatalytic splitting of water or electrolysis but only in those countries with the surplus of hydroenergy. First photocatalytic way of splitting of water was demonstrated by Fujishima and Honda in 1972 [1]. Since that time significant efforts were directed towards search of new photocatalytic materials. At the beginnings it seemed that TiO₂ will be the best photocatalyst for numerous applications. However, relatively high value of band gap of TiO₂ prompted many research groups for search of new semiconducting materials [4-6]. Among these new materials modified or non-modified perovskites, inorganic sulfides, nitrides and oxonitrides represented the best properties for photocatalytic reactions. Simultaneously, the research related with modification of already mentioned materials started to flourish. The main methods of photocatalysts modification are summarized below:

- modification of the oxide surface with noble metals (Pt, Au, Ag, Ni) [7],
- formation of semiconducting composites (eg. CdS-TiO₂) [8],
- sensibilisation of the surface (TiO₂ with adsorbed [Ru(dcpq)₂(dpq)]²⁺ [9],
- doping with metals [10] or anions [11]
- modification of photocatalyst morphology via synthesis of nanostructured materials.

This paper describes the influence of deposition of SnO_x on porous TiO₂ and mesoporous SBA-15 on photocatalytic activity in water splitting.

2 Experimental

2.1 Preparation of photocatalysts

Method I

SBA-15 was prepared according to the procedure described by Zhao et al. [12]. For this synthesis an appropriate amount of block co-polymer PLURONIC -123, tetraethoxysilan and hydrochloric acid were heated in autoclave at 383 K for 20 hours. After removal of template by burning organic substances at 823 K.

The modified titanium –tin sol was prepared by hydrolysis of titanium isopropoxide for 6 hours at 348 K. Next, to such sol an appropriate amount of tin oxide (II) was added providing

TiO₂-SnO ratio as 1.5. After 5 minutes in ultrasound bath this sol solution was introduced to dry SBA-15. The content of TiO₂ in newly prepared SBA-15/ titania structure was 16 wt. %. Final calcinations of these samples were performed at 675 K.

Method II

Titanium isopropoxide was applied during synthesis of mesoporous titania. In standard synthesis the Ti(OC₃H₇)₄ dissolved in ethanol and aged with glucose and HCl for 12 hours. Then, SnO was introduced into obtained gel while vigorously stirring. This procedure was followed by ultrasonification. After drying on air samples were calcined at 606 K.

Method III

Here, 1g of block copolymer of Pluronic 123 was dissolved in ethanol. Than to this solution TiCl₄ was added dropwise and finally appropriate amount of SnO. The obtained sol was gelled for 7 days in air and calcined at 773 K for 5 hours.

2.2 Photocatalytic measurements

Photocatalytic reactor consisted from Quickfit[®] round bottom bulb equipped with reflux. The 0.1 g of photocatalyst was placed in 250 cm³ of water containing 5 cm³ of methanol. Four Vitalux bulbs from Osram served as the source of light (spectral characteristic close to the sunlight). The amount of photogenerated hydrogen was measured chromatographically (Varian 388 equipped with carbon column and TCD).

All samples were characterized with thermogravimetry, low-angle and regular XRD spectroscopy, DRIFT and DRUV spectroscopies. Occasionally TEM and SEM micrographs were recorded. For surface area and porosity measurements low temperature adsorption of nitrogen (77K) was performed.

3 Results and Discussion

The results of surface area, porosity of pure supports and those with supported SnO are presented in Table 1.

Table 1: Characteristic of the applied supports.

Materials	Surface area [m ² /g]	Pore volume [cm ³ /g]	Pore diameter [nm]
SBA-15	821	1,03	6,1
SBA16zolSnO	610	0,80	5,8
TiO ₂ /SnO glu.	118	0,15	5,2
TiO ₂ /SnO	108	0,25	7,2

The drop in surface area and porosity after deposition of titania-SnO sol shows that majority of this sol is located inside the porous structure of SBA-15. Adsorption-desorption isotherms of N₂ (see Figure 1) clearly confirm this assumption.

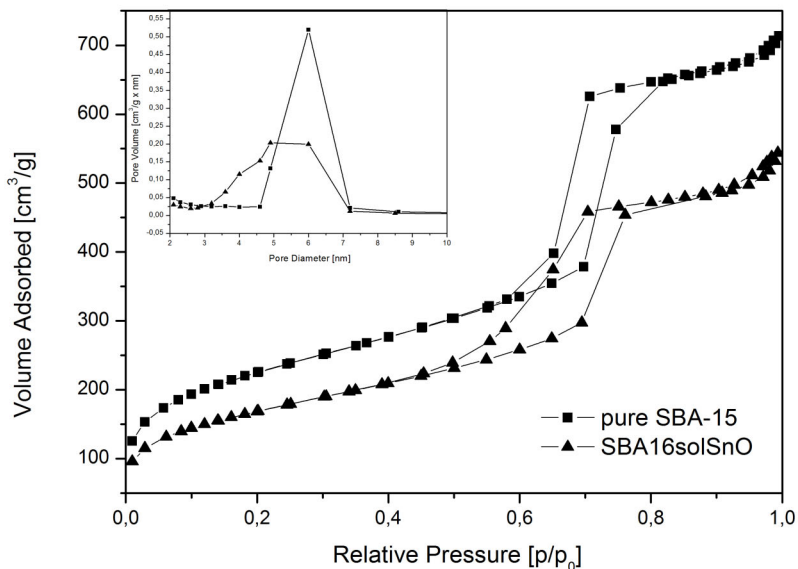


Figure 1: Adsorption-desorption isotherms of N2 at 77K.

In both cases (pure and modified siliceous material) the presence of mesopores is demonstrated by hysteresis loop in the range of p/p_0 equal 0.5 to 0.8. Moreover, the microporous system remained almost untouched after deposition of SnO. This property provides excellent diffusion in the system both liquid as well as evolved gases.

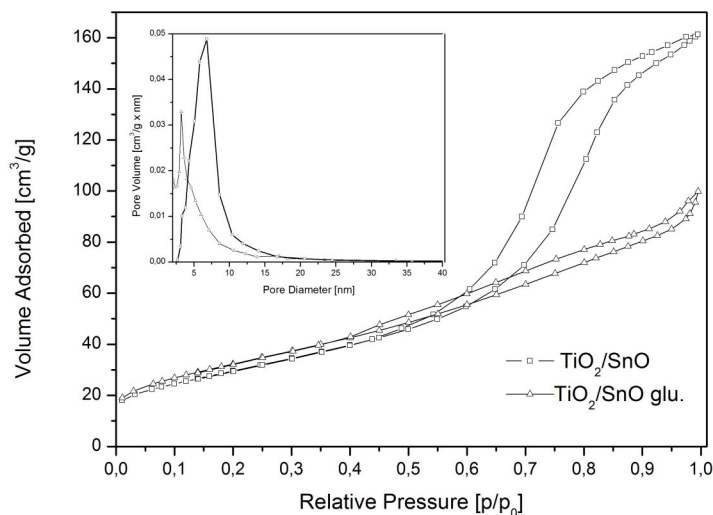


Figure 2: Adsorption-desorption isotherms of N₂ at 77 K for TiO₂ based materials.

Completely different situation can be observed when titania, instead of SBA-15, was applied as the support for SnO. The shape of isotherms as well as the results of surface area values clearly indicate that deposited SnO will represent different character than in SBA-15.

The DRUV-vis spectra of the studied systems are shown on Figure 3. It is obvious that each system is characterized by different ability of electron excitation and in consequence the value of the band gap is different for each studied photocatalyst.

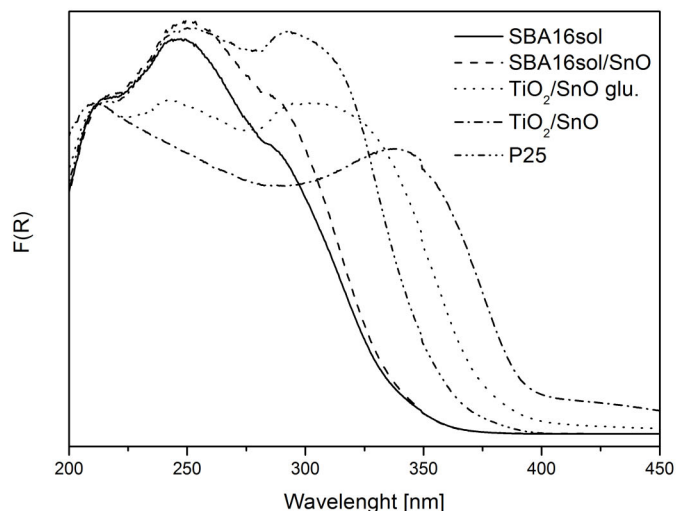


Figure 3: DRUV-vis spectra of the studied photocatalysts.

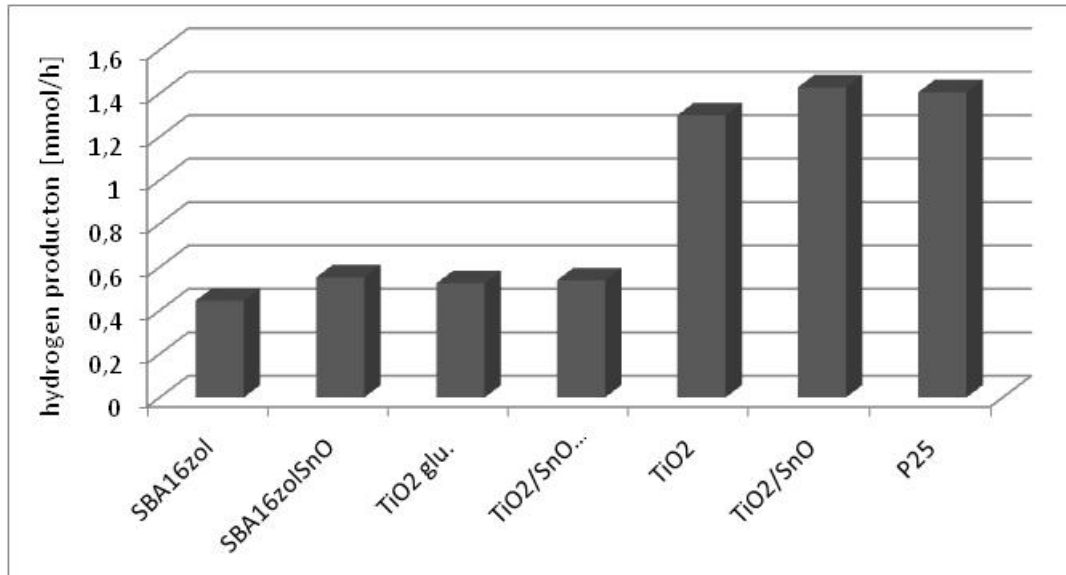


Figure 4: Hydrogen generated over different photocatalysts.

Results presented on Figure 4 show that attempts to increase photocatalytic activity only in one case were successful. Sample prepared according to the method III show the best activity and addition of SnO slightly increase the amount of generated hydrogen. An addition of Sn²⁺ ions influences the ability of light absorption at higher wavelength values. Samples

prepared according to method III show constant progress in hydrogen evolution and an increase of SnO concentration can improve the yield of the studied process.

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