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Modified Titanate Perovskites in Photocatalytic Water Splitting

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1 Introduction

The present world is energy dependant as never it was before. The continuous demand for increased energy production results in significant depletion of the environment. Almost 80 % of generated energy comes from fossil fuels [1]. The significant amounts of greenhouse gases, contamination of air, generation of all kinds of wastes and generation of tremendous amounts of ashes are the final effects of application fossil fuels and to some extent also nuclear energy. One of the possible solutions to minimize and to avoid this scenario is the application of hydrogen as the energy carrier – a universal and ecological fuel [2,3]. Presently, except for electrolysis hydrogen is generated basically from fossil fuels. The photocatalytic splitting of water one day can become the alternative solution to the traditional methods. Since the early seventies of XX century significant efforts have been directed towards extension of this method. Different photocatalysts and their modifications were tested under different conditions both in laboratories and under natural sunlight illumination. Titania and simple perovskites became the well known photocatalysts but their activity is limited only to ultraviolet part of the solar spectrum. Energy required for electron excitation in these materials is relatively high (3.2 eV). Typical perovskites can be obtained in different ways but the most popular is based on reaction of titania and other oxides or carbonates in solid state reactions at high temperatures (>1200 °C). This method provides significant amounts of the required product with uniform dimensions of particles [4]. The main drawback of this method relay on low surface area of the obtained solids; usually close to 1 m^2/g. Low surface area of such perovskites is an obstacle in good dispersion during deposition of platinum or nickel and in consequence leads towards low quantum yield during splitting of water. Thanks to the method of synthesis of perovskites applied in this paper, the obtained solids posses much higher surface area. This effect was attained by lowering significantly temperature of the synthesis. Moreover, the applied method is much simple than in other methods, eg. MBE [5,6] or CVD [7].

2 Experimental

Synthesis performed in this paper represents the modification of synthesis proposed by McLaren and Ponton [8]. The procedure initially proposed for synthesis of barium titanate was also applied for formation of strontium and calcium titanates. Here, for the synthesis barium, strontium or calcium acetates (Sigma-Aldrich), titanium isopropoxide (Ti-isoPrOH) and 1M solution of the organic base (tetramethyl hydroxylamine –TMHA from Sigma Aldrich) were applied.

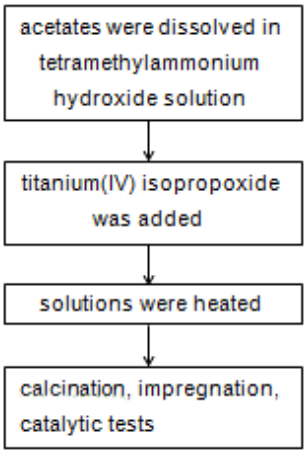

Figure 1: Experimental procedure.

Scheme from Figure 1 shows the basic steps in preparation procedure. In the first step an appropriate acetate was dissolved at room temperature in water solution of TMHA. The ratio of OH- ions to metal ions in all cases was equal 4:1. In the next step the titanium ispropoxide was added while continuously stirring. The molar ratio of Ti-isoPrOH to acetate was like 1:1. After 5 minutes the suspension was heated up to 80 °C and kept at this temperature for 4 hours. After filtration the obtained white powders were washed with distilled water, dried at room temperature and finally calcined. The minimum of calcinations temperature (500 °C) was established on the basis of thermogravimetric measurements.

Samples after characterization with XRD and adsorption-desorption of N_2 at minus 196 °C were impregnated with chloroplatinic acid. Three different concentration of chloroplatinic acids provided 0.5, 0.1 and 0.01 wt. % of platinum on the surface of the perovskites. The incipient wetness method was applied for impregnations.

Photocatalytic test in splitting of water were carried out in photoreactor (from Pyrex glass) with capacity of 250 cm^3. The water-methanol mixture (molar ratio 50:1) with suspended catalyst (0.1 g) was illuminated with 4 Vitalux bulbs from Osram. Temperature of the reaction was 50 °C. The amount of evolved gases was determined applying gas chromatography (Varian 3800 equipped with CarboPlot capillary column).

3 Results

Thermogravimetric experiments with air-dried samples showed that 500 °C is the lowest possible temperature for calcinations. Water, acetic acid and carbon oxides were the main gaseous products during temperature increase. Above 500 °C no further decomposition occurs and this was demonstrated by essential lack of the weight loss. Surface area (BET) of the obtained perovskites is high in comparison with those observed for ceramic method. Pore volume (BJH), except calcium titanate is rather small. Data presented in Table 1 summarize surface properties of the obtained materials.

Table 1: Surface area of received samples.

	Area [m^2/g]	Pore volume [cm^3/g]	Pore diameter [nm]
Sample	Calcination 500°C		
$CaTiO_3$	109.1	0.31	10.9
$SrTiO_3$	23.9	0.08	17.3
$BaTiO_3$	25.7	0.06	10.7
Sample	Calcination 700°C		
$CaTiO_3$	37.9	0.21	25.7
$SrTiO_3$	18.6	0.07	17.7
$BaTiO_3$	12.6	0.05	20.0

Crystal structure of the obtained perovskites was determined with powder XRD technique. In the case of calcium titanate it was found that calcination at 500 °C is not sufficient to create the appropriate structure of perovskite (see Figure 2). The other two materials showed the structure of regular perovskite after calcinations at this temperature. For calcium titanate the appropriate pervoskite type structure appeared after calcination at 700 °C. Here, the presence of reflexes at 33°, 48° and 59° of 2 θ indicates formation of $CaTiO_3$ with slightly increased dimensions of crystals, when compared to standard.

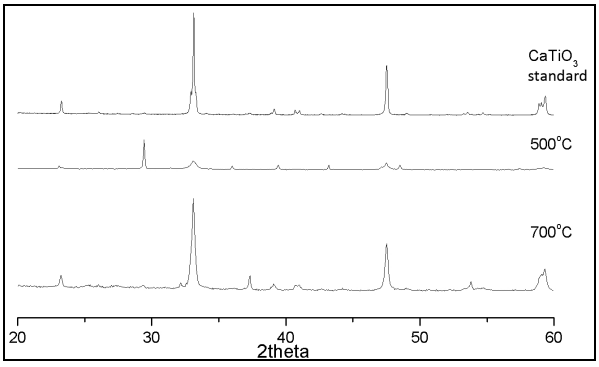

Figure 2: Powder X-ray diffraction pattern, $CaTiO_3$.

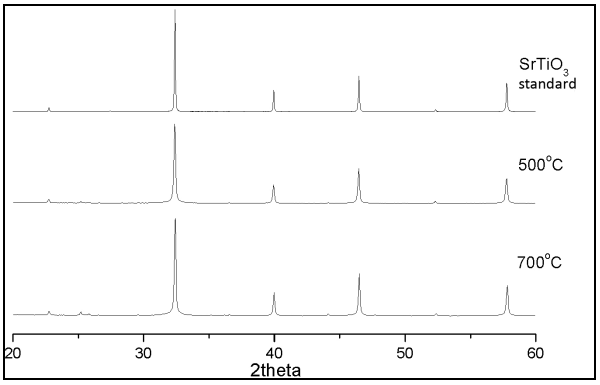

Figure 3: Powder X-ray diffraction pattern, $SrTiO_3$.

Diffraction patterns for strontium titanate shown on figure 3 indicate that appropriate structure of perovskite is already present after calcination at 500 °C. Well defined, narrow reflexes are indicative for small, well crystallized material. The X-ray diffraction patterns of $BaTiO_3$ (see Figure 4) are also well defined after calcination at 500 °C, however, less precise than in the case of $SrTiO_3$.

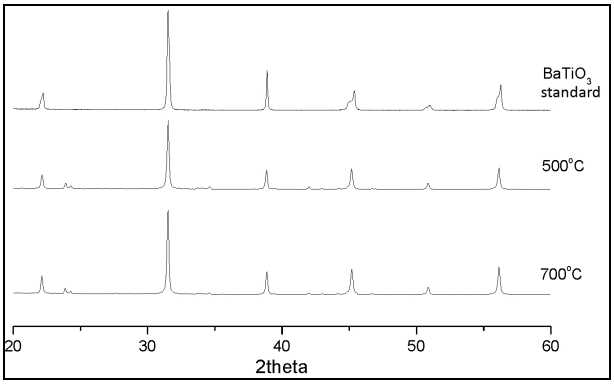

Figure 4: Powder X-ray diffraction pattern, $BaTiO_3$.

The confirmation of the results obtained during XRD measurements In part can be confirmed by SEM microphotographs.

All SEM micrographs (Figure 5) show the same shape and dimensions for the obtained materials. Small dimensions of the obtained semiconductors can be very useful in photocalytic processes while working with suspensions.

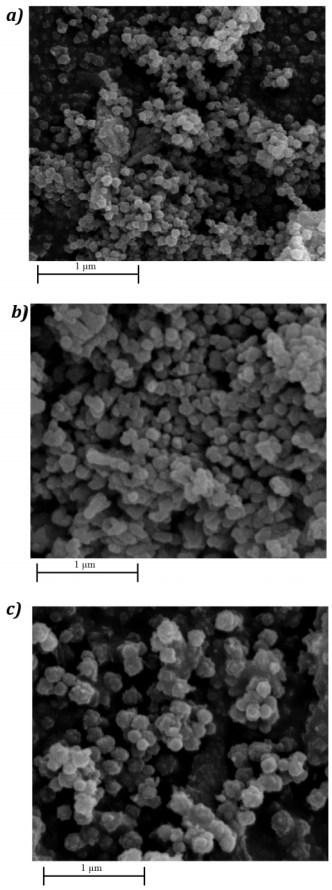

Figure 5: SEM images of perovskites: a) $CaTiO_3$, b) $BaTiO_3$, c) $SrTiO_3$; calcined in 700°C.

In all studied photocatalysts with deposited noble metal the dispersion of these metals was measured. Data for materials containing 0.5 wt. % of platinum and calcined at 700 °C are shown in Table 2. Here, the dispersion was the highest for $CaTiO_3$, and lower for two other. The influence of surface area is here easily observable.

Catalytic activity in water splitting was observed in all studied cases but the best activity was obtained for samples calcined at 700 °C and containing 0.1 wt. % of platinum. Calcium perovskites showed the best performance.

Table 2: Dispersion of platinum (0.5% Pt, calcination 700°C).

Sample	**$CaTiO_3$**	**$SrTiO_3$**	**$BaTiO_3$**
Dispersion [%]	55.6	44.5	38.9

The results for one series of non-modified perovskites are shown on Table 3. These data indicate that performance of calcium titanate containing 0.1 wt. % of platinum is the best. Samples activated at 500°C showed photocatalytic activity, but the amounts of generated hydrogen were much smaller. It was found that for presented perovskites the amount of deposited platinum should be 0.1 wt. %. Too high concentration leads towards formation of large platinum clusters and in consequence a screening effect can be involved.

Table 3. Platinum content and hydrogen evolution.

Sample	**Amount of Pt [% of weight]**	**H_2 [µmol · h^{-1} · g_{cat}^{-1}]**
$CaTiO_3$	0.5	443
	0.1	481
	0.02	371
$SrTiO_3$	0.5	262
	0.1	110
	0.02	102
$BaTiO_3$	0.5	106
	0.1	197
	0.02	trace

4 Summary

Received materials have structure of perovskite, what was shown by XRD diffraction patterns. Perovskite structure is present in all samples with strontium, barium and one sample with calcium. Moreover, received barium and strontium titanate are very similar to pattern materials. XRD results show, that temperature 500°C is too low to create perovskite structure in $CaTiO_3$. However, it is high enough in case of $SrTiO_3$ and $BaTiO_3$. One regularity is obvious, surface area increases for samples calcined in lower temperature. There is a connection between surface area and dispersion of platinum. Both of them reach the greatest value to the calcium titanate.

Catalytic activity was shown by all of received samples. Measurable values were received to samples calcined in 700°C. Calcium titanate had the best catalytic activity, both an amount of

hydrogen and a ratio of hydrogen to platinum. There is one regularity to all samples, the ration of hydrogen to platinum increase when amount of platinum decrease.

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