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Synthesis and characterization of mesoporous Ta_2O_5–TiO_2 photocatalysts for water splitting

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ABSTRACT

Two series of Ta_2O_5–TiO_2 photocatalysts (Ta:Ti = 4:1, 1:1 and 1:4) were prepared by sol–gel technique applying triblock copolymer of Pluronic P123 and were tested in platinized form (0.3 wt.%) in photodecomposition of water under ultraviolet and visible light ($\lambda > 300$ nm). It was found the mesoporous character of tantalum containing catalysts with relatively high surface area (~100–130 $m^2 g^{-1}$) of these samples. However, higher concentration of TiO_2 in mixed oxides leads to the destruction of mesoporous character of synthesized photocatalysts. All samples were characterized with thermogravimetry, XRD, N_2 physisorption, DR-UV–vis and FTIR spectroscopy. The mixed oxides of Ta_2O_5–TiO_2 system showed much lower band-gap than pure Ta_2O_5 and relatively high activity in platinized state in photocatalytic hydrogen generation under visible. Doping of pure oxides and mixed systems with sulfur resulted in lowering of the band-gap values below 3 eV and much better activity in H_2 evolution reaction. Non-platinized photocatalysts showed activity in liquid phase cyclohexene photooxidation at 305 K.

1. Introduction

Due to the world depletion of such energy sources like natural gas and oil, as well as coal with low sulfur content, it is necessary to search for new energy sources and energy carriers. Experts around the world expect prices to continue to spiral upwards in the future, placing considerable pressure of cost of living. The impact of greenhouse gases on global climate changes, especially CO_2, is creating increasing concern among scientists, politicians, business leaders and general public. It is predicted that the appetite for energy will reach 28 TW in 2030 assuming world population of 9 billion people. How to overcome the approaching problem of energy shortage? Hydrogen can be the answer. Among many different alternative fuels (e.g. biofuels, dimethyl ether) hydrogen is forecast to become one of major energy source of the future. Although steam–methane reforming (SMR) and water–gas shift (WGS) reactions are presently the major methods of hydrogen generation for large scale industrial applications [1], many laboratories started the research of alternative routes of hydrogen generation since early seventies of XX century. Unexpected progress in fuel cells development triggered search for new methods of this most energetically efficient fuel.

Among many new “green” methods hydrogen generation a specific place takes a photocatalytic splitting of water. Since discovery of photoelectrochemical splitting of water by Fujishima and Honda [2], photocatalytic generation of water attracts much attention. The majority of already tested semiconducting materials operate in the ultraviolet part of the light spectrum. Assuming that sunlight will be used as the source of excitation it is necessary to develop such photocatalysts for water splitting that can apply visible light. Ultraviolet part of the solar spectrum do not exceed 2–3%, visible region is close to 40% whereas the remaining part represents infrared radiation. Moreover, the major drawback associated with application of semiconducting photocatalysts rely on the high energy required for electron photoexcitation and fast recombination between light excited electrons and positively charges holes. Therefore, finding of the materials, which can overcome these obstacles and can operate under visible radiation is the main challenge in hydrogen generation *via* photocatalytic splitting of water.

The possibility of application of pure mesoporous Ta_2O_5 as the photocatalyst in water splitting under ultraviolet irradiation was demonstrated by the group of Domen [3–5]. It is known that surface area in photocatalysts plays a minor role in their activity, however, in the case of metal supported photocatalysts too low

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surface area can lead towards poor dispersion of metal and screening effects. Presence of such metals like platinum or nickel causes much faster transfer of excited electrons towards surface of semiconductor, lowering simultaneously negative effect of fast recombination. On the other hand screening effects can significantly decrease photacatalytic activity due to limited access of light to semiconductor. Therefore, enlarged surface area of photocatalysts can also influence the efficiency of applied semiconductors.

Present paper presents synthesis of mesoporous tantalum–titanium oxide systems with relatively high surface area with different Ta:Ti ratio. These materials were applied as photocatalysts for water splitting and were doped with platinum. The extension of photoactivity towards visible region of light spectrum was realized by doping these semiconducting systems with sulfur.

2. Experimental

Two series of Ta_2O_5–TiO_2 samples were prepared from Ti–*iso*PrOH or $TiCl_4$, respectively. In both series $TaCl_5$ was applied as the source of tantalum. Pure mesoporous tantalum oxide was obtained *via* hydrolysis of 0.01 M ethanol solution of tantalum pentachloride according to the procedure described by Yang et al. [6]. The mixed oxides were obtained by hydrolysis of the respective salts in appropriate ratio of Ta^{5+} and Ti^{4+} ions from ethanol solutions containing triblock copolymer of Pluronic P123. After addition of appropriate amounts of Ti–*iso*PrOH or $TiCl_4$ into 12.5 cm^3 of anhydrous ethanol of Pluronic P123 it was added the required amount of $TaCl_5$. After the intense mixing for 90 min a hydrolysis was performed for 24 h at room temperature on Petri dishes in closed vessel under autogenic pressure of water vapor. The obtained opalescent sols were next gelated for 7 days at 415 K, followed by 5 h calcinations at 825 K. Pure TiO_2 was obtained analogously by hydrolysis either of Ti–PrOH or $TiCl_4$ instead of $TaCl_5$. Thus, pure mesoporous Ta_2O_5 (catalyst-A), samples with different molar ratio of Ta and Ti (Ta:Ti = 4:1 (catalysts-B), Ta:Ti = 1:1 (catalyst-C), Ta:Ti = 1:4 (catalyst-D) and pure TiO_2 (catalysts-E) for each titanium precursor were obtained (see Table 1). Samples obtained from titanium chloride are marked with asterisk (e.g. D*, E*). For comparison the hydrated forms of Ta_2O_5 and TiO_2 were precipitated with ammonia solution (12.5%) till pH 9 was reached. The obtained oxides were platinized with water solution of chloroplatinic acid and the amount of supported platinum was adjusted to 0.3 wt.%. Samples containing S were prepared by impregnations of the calcined oxides with thiourea solutions.

Table 1
BET surface area and porosity of Ta_2O_5–TiO_2 system

Sample		BET surface area ($m^2\ g^{-1}$)		Pore size diameter BJH (nm)	
		(i)	(Cl)	(i)	(Cl)
$Ta_2O_5(A)^*$		–	43	–	3.7
$Ta_2O_5(A)$		–	113	–	3.6
B(i)	B(Cl)	134	121	3.6	2.8
C(i)	C(Cl)	107	117	7.2	6.5
D(i)	D(Cl)	133	110	5.8	4.9
E(i)	E(Cl)	13	61	13.4	24.4

The prepared samples were characterized with XRD, BET surface area and porosity, UV–vis, FTIR spectroscopy and TEM.

Photocatalytic tests were performed in Pyrex photoreactor under visible and ultraviolet irradiation (>300 nm) applying four 300 W Vitalux bulbs (from Osram). The water–methanol mixture (50:1) was applied in photocatalytic tests of splitting of water (details can be found elsewhere [7]), whereas cyclohexene photooxidation was performed under irradiation of 23 × 10^3 lux.

3. Results and discussion

Thermogravimetric analysis of non-calcined samples allowed to establish the lowest temperature for template removal. Both weight loss measurements and DTA curves (Fig. 1) indicate that total removal of the template can occur at 825 K. This is indicated by strong exothermic effect at ~825 K. The exothermic maximum 580–600 K in both series is related to the removal of the copolymer

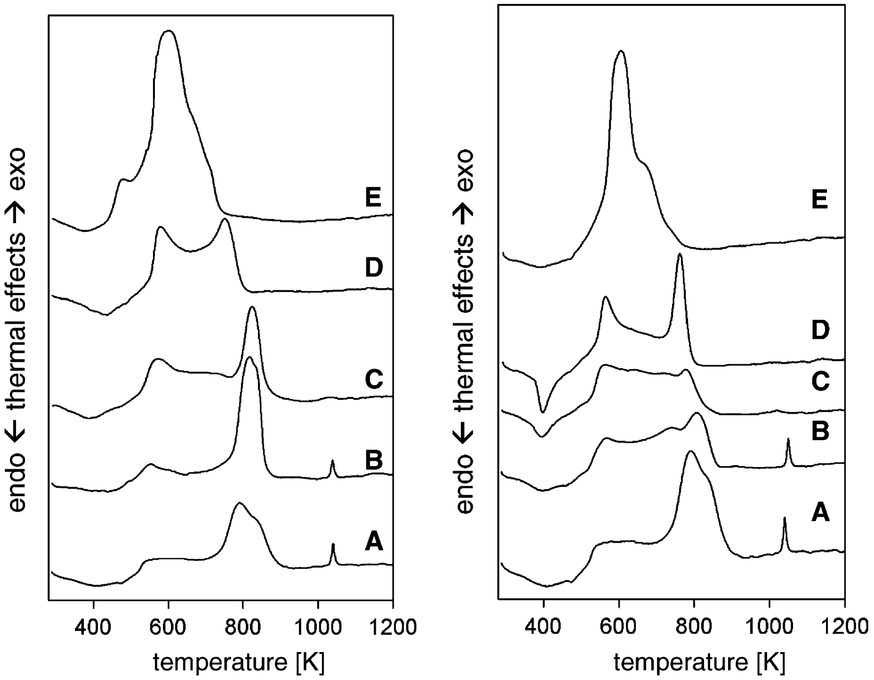

Fig. 1. DTA curves of samples after gelation with Pluronic P-123: left, Ti–*iso*ProH as titanium ions precursor; right, $TiCl_4$ as precursor.

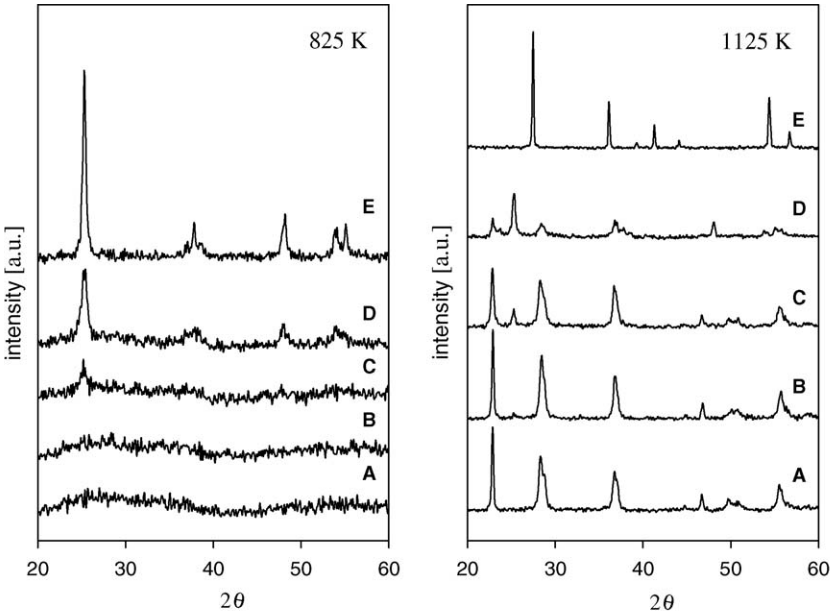

Fig. 2. X-ray diffraction patterns of samples calcined at 825 K (left) and 1125 K (right).

template from the external surface of generated gels, whereas those at 825 K indicate complete escape of P123 from mesoporous structure (compare TEM micrograph in Fig. 3). In the case of pure TiO_2 (curves E in Fig. 1) the complete removal of template was realized at ~570 K. Although, temperature of 825 K is sufficient to generate the carbon-free materials, it is still too low to establish well-defined crystal structure. Diffraction patterns presented in Fig. 2 (left) show the appearance of reflexes characteristic for anatase for samples with Ta:Ti molar ratio equal 1 or lower. At calcination temperature of 825 K only pure TiO_2 indicates well-defined crystal structure (Fig. 2, left). All other samples indicate more or less amorphous character. On the other hand, strong exothermic peak on DTA curves at ~570 K (Fig. 1E) proves that, that formation of mesoporous structure of TiO_2 is rather impossible, because position of this maximum indicates burning of the template at the external surface of titania samples. The absence of the high temperature exothermic maximum at ~825 K is indicative for the absence of template within the mesoporous structure of TiO_2, if any. The low value of surface area of TiO_2 (see Table 1), as well as the shape of nitrogen adsorption–desorption isotherms (Fig. 3) and TEM micrographs confirmed lack of mesoporous structure of pure titania samples. Pure Ta_2O_5 (sample A) and samples with low content of Ti (sample B and B*) are amorphous after calcination at 825 K. Formation of crystalline orthorhombic of Ta_2O_5 was detected on DTA curve as sharp exothermic maximum at 1050 K. The X-ray diffraction patterns of pure oxides and those with different ratio of Ta and Ti after calcinations at 1125 K (Fig. 2, right) show the existence of well-defined structures of orthorhombic Ta_2O_5 (A) and rutile (E) and certain mixed structures (curves C and D). These results indicate that only at low ratio of Ti to Ta the orthorhombic structure can be preserved. At higher concentrations of TiO_2 the appearance of new structure, probably titanium tantalate, is observed.

Mesoporous hexagonal structure of pure Ta_2O_5 obtained with template was established on the basis of nitrogen adsorption–desorption isotherms (type IV), existing characteristic loop, as well as from TEM images (see Fig. 3). An application of $TaCl_5$ and precipitation with ammonia resulted in non-uniform porous system with low surface area. Data presented in Table 1 and in Fig. 4 shows that samples with low TiO_2 content preserve their mesoporous character, whereas the increase of TiO_2 content in these samples causes random distribution of pores with slight increase of surface area (Fig. 4, curves C and D), independently of the titanium ions source. Pure titanium oxide exhibited very low surface area and total absence of mesopores. The obtained results show that applied technique of incorporation of titanium ions into the mesoporous structure of Ta_2O_5 can be used without damage of mesoporous character of tantalia only at high ratio of Ta:Ti. Otherwise another methods must be applied. The alternative route for deposition of titania in mesporous structure of Ta_2O_5 can be realized *via* hydrolysis of alcoholic solution of Ti–*iso*PrOH. Such system has been already successfully applied in our laboratory for deposition of titania over siliceous SBA-15 [8,9].

Diffusion reflectance UV–vis spectra shown in Figs. 5 and 6 indicate characteristic electronic excitation bands of non-doped

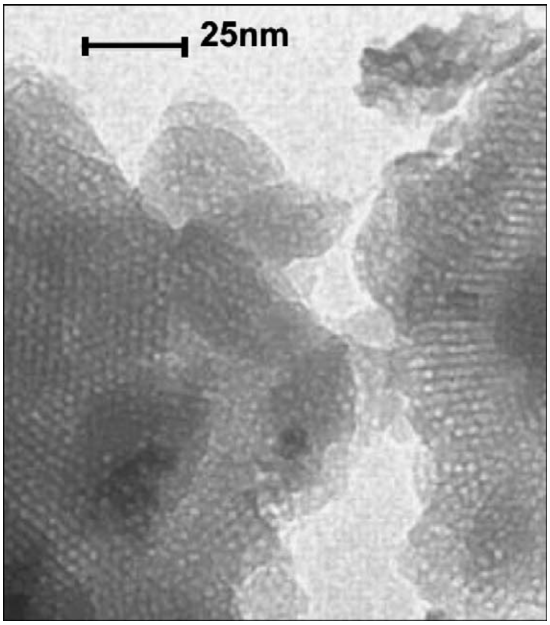

Fig. 3. TEM image of mesoporous Ta_2O_5.

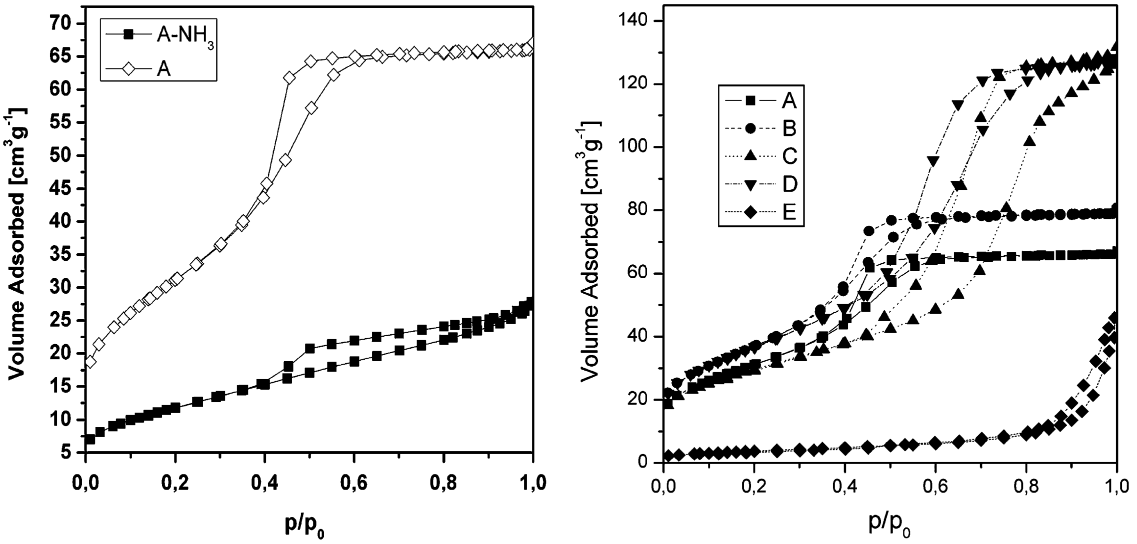

Fig. 4. Nitrogen adsorption–desorption isotherms at 77 K.

Table 2
Energy band-gaps calculated from diffusion reflectance UV–vis spectra

Sample	Band maxima (nm)	Energy band-gap (eV)
Ta_2O_5(A)	280	3.97
S-doped Ta_2O_5	280, 360	2.95
B	280, 345	3.30
C	280, 350	3.19
D	280, 355	3.09
TiO_2(E)	280, 345	3.05
S-doped TiO_2	280, 370, 420	2.90

and sulfur-doped oxides. As it was expected the characteristic band for pure Ta_2O_5 is located deeply in the UV region what corresponds to the band-gap of ~4 eV. This value does not allow for the excitation of electron within visible region of the light and in consequence there was no water splitting observed. Data presented in Table 2, as well as curves in Fig. 5, show that an increase of titania in mixed oxides causes the lowering of the band-gap values (<4 eV) and in consequence better activity in water splitting. However, all photocatalysts with different Ta:Ti ratio can not operate successfully within the visible region of the light. Only doping of these systems with sulfur can shift towards visible the ability of water splitting (Fig. 6). In the case of Ta_2O_5 doping with sulfur caused the decrease of band-gap value for almost 1 eV. Similar effects were found for all other samples, however, the shift of the light absorbance towards visible region was the highest for samples with high Ti:Ta ratio. Although the effect of sulfur or nitrogen doping was studied by different laboratories [10–12] it is still very difficult to explain the location of sulfur in the oxide structure and its influence in the mechanism of water splitting.

All samples containing 0.3 wt.% of Pt were tested in water splitting reaction whereas those without Pt in cyclohexene

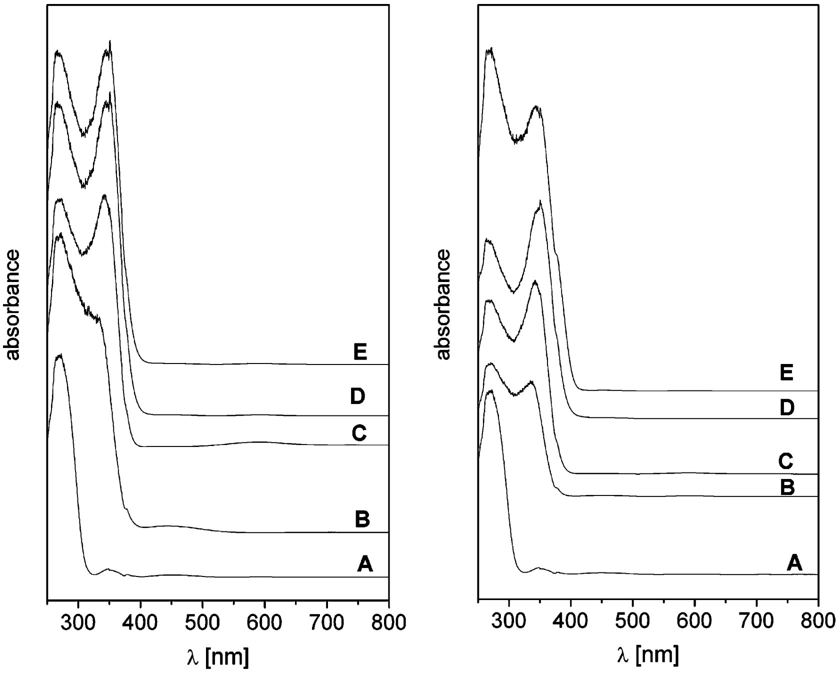

Fig. 5. Diffuse reflectance spectra of Ta_2O_5–TiO_2 systems.

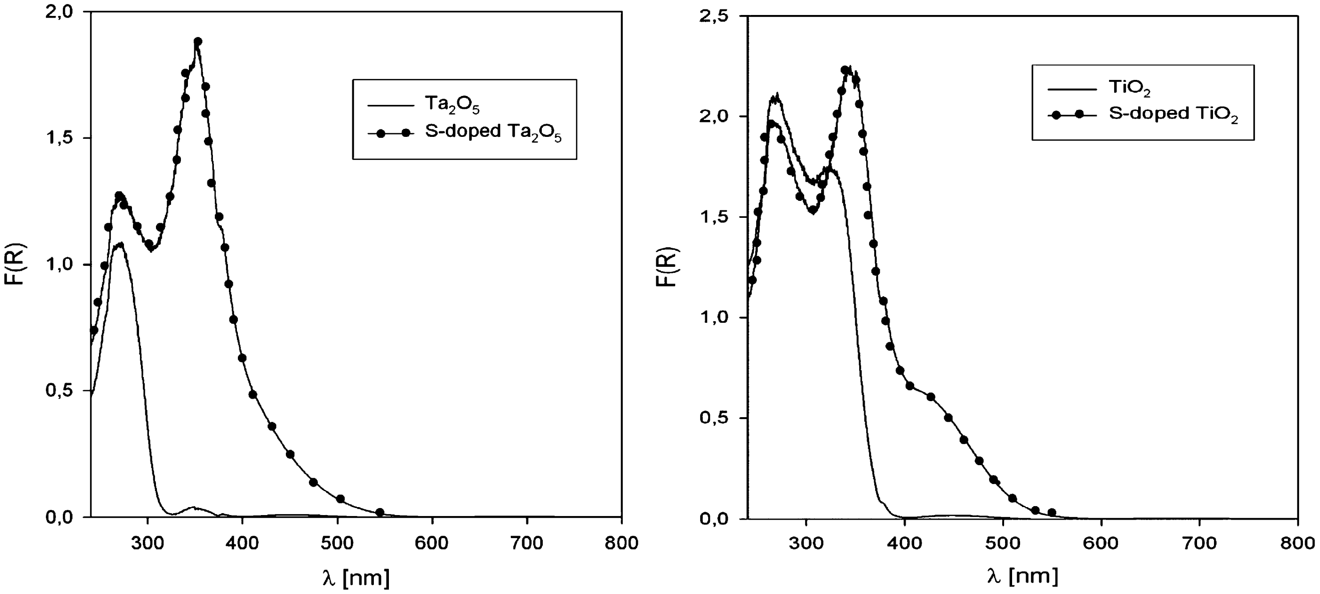

Fig. 6. Diffuse reflectance spectra of S-doped Ta_2O_5 (left) and S-doped TiO_2.

Table 3
Photocatalytic activity in splitting of water at 325 K and photooxidation of cyclohexene at 305 K

Sample	Amount of H_2 evolved (mmol)[a]	Cyclohexene photooxidation				
		Conversion (%)	Selectivity (%)			
			Cyclohexane	Epoxide	Cyclohexanone	Cyclohexanodiol
Ta_2O_5(A)	0.00	18.0	37	2.0	56	8.4
S-doped Ta_2O_5	0.24	–	–	–	–	–
B	0.14	32.7	23	2.4	71	3.8
C	0.03	15.0	56	4.7	33	6.9
D	0.25	24.7	35	3.9	57	3.2
TiO_2(E)	3.52	25.6	31	2.4	61	4.4
S-doped TiO_2	4.55	–	–	–	–	–

[a] Total amount of evolved H_2 after 2 h of reaction.

photooxidation reaction applying hydrogen peroxide and acetonitrile as the solvent. The results of photocatalytic activity are shown in Table 3. Tantalum oxide was completely non-active in water splitting under applied conditions. However, lowering of the energy band-gap from ~4.0 eV of this oxide to values close to 3.3–3.1 eV for Ta_2O_5–TiO_2 systems resulted in appearance of weak activity in water splitting. Moreover, doping with sulfur of both pure oxides increased the amount of the photogenerated hydrogen significantly. Preliminary experiments with mixed oxides doped with sulfur showed significantly improved activity in comparison with those undoped.

All non-platinized photocatalysts indicated catalytic activity in cyclohexene oxidation at 305 K (see Table 3). Although the obtained conversions do not indicate any regularity, the presence of cyclohexanone in the products of this reaction indicate that different mechanism is engaged in photocatalytic reaction [13] and that further studies are required to elucidate the details. In contrast, in the same reaction performed under similar conditions but without irradiation resulted in complete absence of cyclohexanone and very different selectivities.

Recent paper by Kondo and Domen [14] showed that enhancement of photocatalytic activity in total decomposition of water require better crystallinity of the mesoporous Ta_2O_5. The same effect is expected for the systems presented in this paper and further works are under way.

4. Conclusions

Modification of mesoporous Ta_2O_5 with titania applying template technique of synthesis with neutral block copolymer can be performed up to Ta to Ti molar ratio 4:1 without loosing mesoporous character of these materials. At higher concentration of titania, in the studied mixed oxides, a constant decrease of mesoporous structure was found. Doping of the studied systems with sulfur resulted in lowering of the band-gap values these systems and in consequence higher activity in H_2 evolution reaction under visible.

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References

[1] J.N. Armor, Appl. Catal. A: Gen. 176 (1999) 159.
[2] A. Fujishima, K. Honda, Nature 37 (1972) 238.

[3] Y. Takahara, J.N. Kondo, T. Takata, D. Lu, K. Domen, Chem. Mater. 13 (2001) 1194.

[4] J.N. Kondo, M. Uchida, K. Nakajima, L. Daling, M. Hara, K. Domen, Chem. Mater. 16 (2004) 4304.

[5] R. Nakajima, D. Lu, M. Hara, K. Domen, J.N. Kondo, Stud. Surf. Sci. Catal. 158 (2005) 1477.

[6] P. Yang, D. Zhao, D.I. Mergolese, B.F. Chmelka, G.D. Stucky, Chem. Mater. 11 (1999) 2813.

[7] M. Zalas, M. Laniecki, Sol. Energy Mater. Sol. Cells 89 (2005) 287.

[8] M. Wójtowski, M. Laniecki, Stud. Surf. Sci. Catal. 158 (2005) 757.

[9] M. Ruszel, B. Grzybowska, M. Laniecki, M. Wójtowski, Catal. Commun. 8 (2007) 1284.

[10] T. Ohno, M. Akiyoshi, T. Umebayashi, K. Asai, T. Mitsui, M. Matsumura, Appl. Catal. A: Gen. 265 (2004) 115.

[11] T. Ihara, M. Miyoshi, Y. Iriyama, O. Matsumoto, S. Sugihara, Appl. Catal. B: Environ. 42 (2003) 403.

[12] S. Sakthivel, H. Kisch, Chemphyschem 4 (2003) 487.

[13] K.L. Antcliff, D.M. Murphy, E. Griffiths, E. Giamello, Phys. Chem. Chem. Phys. 5 (2003) 4306.

[14] J.N. Kondo, K. Domen, Chem. Mater. 20 (2008) 835.