

Supercapacitors and energy conversion structures based on WS₂ and MoS₂ disulfides

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In this paper, disulfides WS₂ and MoS₂ were successfully prepared using thermal decomposition and utilised for fabrication of supercapacitor- and water splitting electrodes. Both, energy storage and conversion performances of these electrodes were compared with electrodes prepared with commercial MoS₂, WS₂, and activated carbon (AC). The electrochemical characterisation confirmed the pseudocapacitive character of disulfide-based supercapacitor electrodes. A strong influence of the scan rate on the specific capacitance was found, which is due to the diffusion of ions and the pseudocapacitive nature of charge storage. A specific capacitance of 405 mF/cm² at 10 mV/s scan rate was achieved on MoS₂ structures prepared by thermal decomposition. This value is 3.5-times greater than the capacitance achieved on commercial MoS₂ and 6.8-times greater than capacitance achieved on structures with activated carbon. A specific capacitance of 396 mF/cm² at 10 mV/s scan rate was achieved on WS₂ structures prepared by thermal decomposition, which was 2.2 and 6.7-times greater than the capacitance achieved on commercial WS₂ and AC based electrodes, respectively. Water-decomposition structures showed greater catalytic activity of thermally decomposed disulfides for HER compared to commercial materials and AC. The study showed a high perspective of MoS₂ and WS₂ prepared by thermal decomposition for energy storage applications by means of supercapacitors and energy conversion through water electrolysis and hydrogen generation.

Key words: MoS₂; WS₂, thermal decomposition, supercapacitor, water electrolysis, hydrogen

1 Introduction

With an ever-growing energy demand, energy conversion and storage have increasingly found their place in the scientific world. The development of a new and cost effective catalyst with a high reaction rate allows efficient and economical utilisation of water electrolysis for conversion of electrical energy to chemical energy stored in hydrogen bonds [1]. Structures for energy storage, mainly supercapacitors (SCs) based on new pseudocapacitive materials, are perspective devices with long service life, great power density and high energy density [2]. Compared to batteries, such supercapacitors have a much higher specific power density (per unit mass) and energy/power efficiency, fast charging/discharging rate and longer lifetime.

Due to the unique graphene-like 2D structure [3], the metal disulfides represent a perspective and recently strongly investigated materials for both, supercapacitor and water splitting applications. Among the transition metal disulfides, wolfram disulfide, WS₂ and molybdenum disulfide, MoS₂ have received much attention in recent years [4-6]. Their structure consists of three atom layers: Mo or W layer sandwiched between two S layers, and these triple layers are stacked and held together by weak van der Waals interactions [7]. The structural benefits of sheets-like 2D disulfides make the ion-transportation easier during the rapid charging and dis-

charging cycles what results in exceptional electrochemical properties [8, 9]. Their energy densities show significantly higher values than carbon electrodes [10]. Replacing Pt with earth-abundant catalysts is one of the most important tasks toward potential large-scale HER applications. Among many potential candidates, low cost, and earth-abundant transition metal dichalcogenides such as MoS₂ and WS₂ have been promising as good H₂ evolution electrocatalysts when they are engineered into the structures with active sites [11].

The production of WS₂ or MoS₂ powder by direct decomposition of tungsten or molybdenum compounds has become an attractive method with a short flow, less pollution and low cost [12]. Structural analysis shows that these materials prepared at a high decomposition temperature exhibit high crystallinity. Liu and his co-workers have demonstrated that the thermal decomposition of ammonium tetrathiomolybdate (NH₄)₂MoS₄ is able to produce high-quality MoS₂ thin layers [13].

Disulfide-based supercapacitors have still not reached the maximum theoretical capacitance and their function mechanism is still not sufficiently explained. In addition, cheap techniques for the preparation of disulfide-based catalysts with high reaction rates as well as a deeper understanding of the catalytic mechanism for water splitting are in strong demand and further investigation is needed. In this work, we focus on the preparation and character-

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ization of supercapacitor- and water splitting electrodes based on MoS₂ and WS₂ disulfides, prepared by thermal decomposition. The electrochemical characterisation is provided to investigate the capacitance behaviour of supercapacitor electrodes at different scan-rates and catalytic behaviour of disulfides for hydrogen and oxygen generation through water splitting. The results are compared and analysed with respect to the structures based on commercially available MoS₂ and WS₂ disulfides.

2 Experimental

WS₂ and MoS₂ powders were prepared by thermal decomposition of ammonium tetratungstate, (NH₄)₂WS₄ and ammonium tetrathiomolybdate, (NH₄)₂MS₄ in a nitrogen atmosphere, respectively. The temperature of 540 ° was controlled in the chamber for 2 hours during the decomposition process. After the decomposition, samples were kept in the nitrogen atmosphere for several hours to cool down to room temperature. X-ray diffraction (XRD) was provided by a D8 Advance diffractometer equipped with Cu anode for high-intensity radiation ($\lambda = 1.5406 \text{ \AA}$)

For comparison reason, the as-prepared disulfides were compared with commercial MoS₂ and WS₂ disulfide powders purchased from Sigma Aldrich. In the paper, the structures prepared with commercial-based powders have notation Comm and structures prepared with thermally decomposed disulfides have notation TD.

The fabrication of supercapacitor electrodes was carried out as follows: The selected as-prepared or commercial disulfide, AC and poly(tetrafluoroethylene) (PTFE) were mixed in a weight ratio of 45:45:10 with a stirrer shaft. For comparison reason, a supercapacitor electrode with AC and PTFE in the weight ratio 90:10 was prepared as a reference sample. The weight of these substances was measured by precision balance VWR SM425i. The resulting gel was coated onto the Cu with activated carbon substrate by Dr Blade technique, followed by drying at room temperature for 24 h on air. The constant

area of all the characterized electrodes was ensured by a circular press with a 14 mm diameter.

The fabrication of electrochemical electrodes for water splitting was carried in a similar matter as described above. The as-prepared or commercial disulfide, AC and nafion used for such structures as a binder were mixed in a weight ratio of 45:45:10 with stirrer shaft. The resulting gel was coated onto the Cu metal plate by Dr Blade technique, followed by drying at room temperature for 24 h on air. The area was defined by the epoxy resin, which provided protection of the metal electrode from the harsh electrolyte environment.

All electrochemical measurements were done in three-electrode setup measured by a Gamry potentiostat Interface 1010 E, where supercapacitor- or water splitting electrodes acted as a working electrode, Pt electrode as a counter electrode, and Ag/AgCl as a reference electrode. The electrochemical measurements of supercapacitor electrodes were carried out in 1 M KCl aqueous electrolyte with pH 7 using cyclic voltammetry (CV). CV scans were done between -0.6 and 0.1 V at different scan-rates, v . The specific capacitance was calculated in F/cm². The CV scans were used for the calculation of specific capacitance, as a function of v ,

$$C_s = \frac{\int I(V)dV}{v\Delta VS}, \quad (1)$$

where ΔV is the voltage window, v is the scan-rate and S is the active area of the sample.

The electrochemical measurements of water splitting electrodes were carried out in 1 M KOH aqueous electrolyte with pH 14 in the voltage range from -0.5 V to 1.9 V. The obtained data were plotted with x -axis as voltage vs reversible hydrogen electrode (RHE).

3 Results and discussion

3.1 XRD characterization

Thermally decomposed powders were examined by XRD to confirm the presence of MoS₂ and WS₂. Figure 1 shows the XRD patterns of the WS₂ and MoS₂

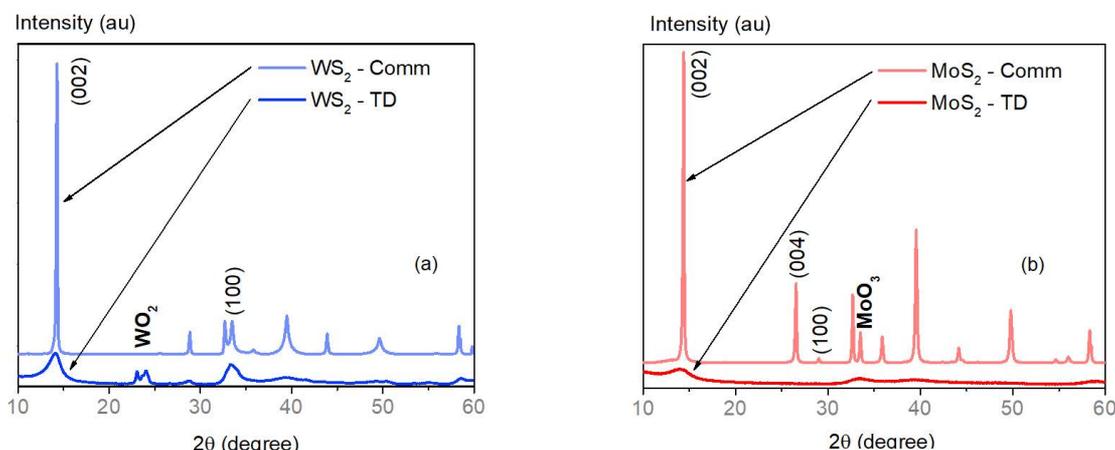


Fig. 1. XRD pattern of commercial and thermally decomposed powders of: (a) – WS₂, and (b) – MoS₂

powders prepared by thermal decomposition in comparison with the commercial ones. The XRD pattern of the commercial disulfides shows the presence of sharp crystalline peaks indicating their high order of crystallinity [14]. The XRD pattern of thermally decomposed disulfides shows the presence of wider diffraction peaks. For WS₂, peaks are observed at $2\theta = 13.23^\circ$ and 33.65° that arises from the (002) and (100) faces of WS₂. For MoS₂, peaks are observed at $2\theta = 13.23^\circ$, 25.62° and 28.51° that arises from the (002), (004) and (100) faces of hexagonal MoS₂. The low intense peak for nanocrystalline nature is beneficial for the easy electrolyte ions interaction with the electrode [15]. Thermally decomposed disulfides also exhibited the presence of WO₂ and MoO₃ oxides for WS₂ and MoS₂ powders, respectively. The origin of such oxides will be the subject of further study.

3.2 Supercapacitor electrodes

The first part of the study is dedicated to the characterisation of supercapacitor electrodes. Electrochemical cyclic voltammetry measurements were performed to examine the capacitance properties of prepared electrode structures. Figure 2(a) shows CV scans taken at 50 mV/s scan-rate of the as-prepared supercapacitor electrodes with commercial MoS₂ and WS₂ disulfides, and those prepared by thermal decomposition. Results revealed a significant hysteresis of all CV curves, which is an indication of the charge storage mechanism in structures. All disulfides revealed a higher hysteresis compared to AC-based electrodes, which supports the high perspective of disulfides for the preparation of supercapacitors with high capacitance. By comparison of the electrodes with commercial and thermally decomposed disulfides, the higher hysteresis and therefore higher capacitance is observed for the TD type for both MoS₂ and WS₂ materials. Figure 2(b) shows specific capacitance extracted from CV scans at different scan-rates. Electrodes with thermally decomposed MoS₂ and WS₂ exhibit high specific capacitance of 405 mF/cm² and 396 mF/cm² at 10 mV/s, respectively. These values are significantly higher compared to 116 mF/cm² and 180 mF/cm² obtained on commercial MoS₂- and WS₂-based electrodes, or 59 mF/cm² obtained on activated carbon electrodes, respectively. Results revealed an increased specific capacitance with decreasing v for all the disulfide-based supercapacitor electrodes and structures with activated carbon. This behaviour can be associated with two mechanisms: (i) slow diffusion of ions from the electrolyte to the surface of the electrode and to the micropores in the electrode, and (ii) Faradaic charge storage mechanism based on reversible reactions, which is presented for materials with pseudocapacitive properties [16]. A smaller increase of the specific capacitance for AC-based structure upon the decrease of v is due to the dominant electrical double layer capacitance (EDLC) storage mechanism. EDLC mechanism is typically presented for supercapacitors with carbon materials [17]. For such type of storage mechanism, diffusion of ions alone influences the specific capacitance at low v .

Figure 3(a) shows the CV current extracted at -0.4 V plotted as a function of the square root of v to gain insight into the charge storage mechanism of disulfide-based electrodes. The linear behaviour of these curves revealed a dominant pseudocapacitive mechanism of charge storage for prepared supercapacitor structures with MoS₂ and WS₂. This supports the presence of the Faradaic charge storage mechanism and its influence on the high increase of specific capacitance for disulfide materials observed from the presented results.

The important factor for specific capacitance at low v is the surface morphology and the presence of micropores in the structure. Small pores in the electrode are accessible by ions only at slow v and hence result in the higher value of the specific capacitance or slow charging and discharging. The presence of pores and overall surface area of an active electrode hence plays an important role during electrochemical charge storage. That means high surface area facilitates maximum active sites for charge storage and as a result, enhanced supercapacitive parameters will be obtained. The question for the next analysis was, whether the increase of the specific capacitance observed on thermally decomposed disulfides was associated with the increase of the pores density in the electrode. For this purpose, the morphological factor (φ) of electrodes was extracted. Figure 3(b) shows the current density at -0.4 V as a function of scan-rate. These dependencies can be correlated with the morphology of porous structures. The difference in the C_d and $C_{d,e}$ slopes observed in Fig. 3(b) with the slower scan-rates is caused by the presence of surface areas located in the more difficult-to-access regions. This effect is caused due to the slow ionic charging process within the higher scan-rates, where ions in the electrolyte are not capable of reaching the more difficult-to-access regions of the structure. As shown in Fig 3(b), two linear segments are observed, which represent differential capacitance (C_d) and external differential capacitance ($C_{d,e}$) of the structure. Morphological factor (φ) can be defined as the ratio of the internal (S_i) and total (S) surface areas [12], with the differential capacitances $C_{d,i}$ and C_d representing the differential capacitance of the internal and total surface areas of the structure

$$\varphi = \frac{S_i}{S} = \frac{C_{d,i}}{C_d} = \frac{C_d - C_{d,e}}{C_d} = 1 - \frac{C_{d,e}}{C_d}, \quad (2)$$

where, $C_d = C_{d,e} + C_{d,i}$.

The morphology factor can be described as the ratio of the difficult-to-access region in the structure to the overall topography of the structure, where a higher number indicates a higher morphology. Table 1 shows the extracted parameters for all structures. All disulfide based electrodes exhibited a higher φ compared to AC-based structures, which indicates higher surface area and morphology of these electrodes. The increase of (φ) using thermally decomposed WS₂ in comparison with a commercial one indicates a higher number of difficult to access pores in this TD structure. However, no significant

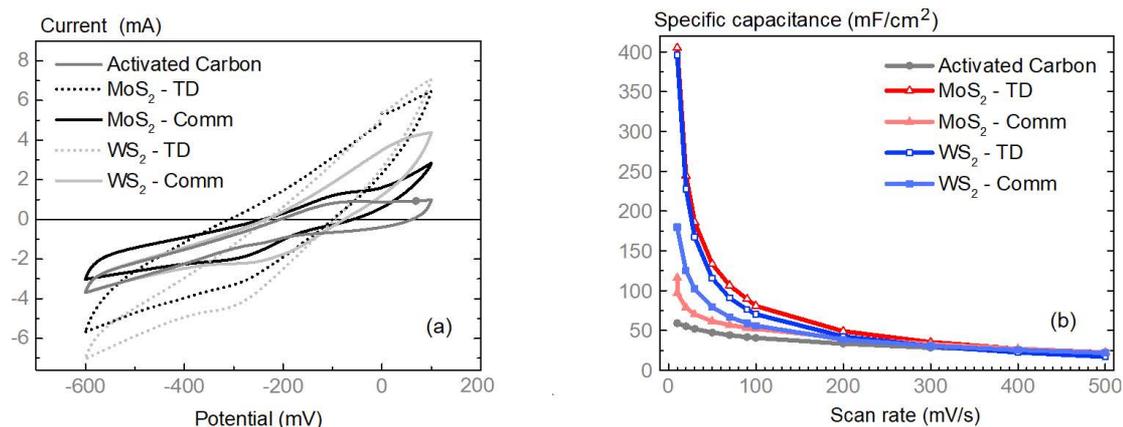


Fig. 2. (a) – cyclic voltammetry curves of different samples in 1 M KCl aqueous electrolyte at scan-rate, $v = 50$ mV/s, and (b) – variation of specific capacitance as a function of scan-rate calculated from CV measurements

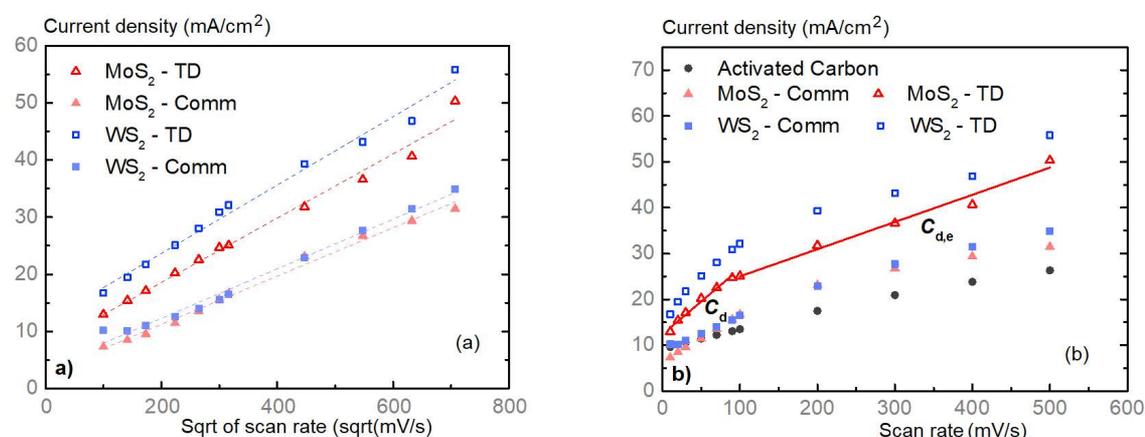


Fig. 3. (a) – current extracted from CVs at $V = -0,4$ V as function of a square root of scan rate, v , and (b) – scan-rate, v for disulfide structures

Table 1. Morphology factor φ calculated from current density vs scan-rate

Samples	(φ)
Activated Carbon	0.26
WS ₂ Commercial (Comm)	0.33
WS ₂ - Thermal Decomposition (TD)	0.70
MoS ₂ - Commercial (Comm)	0.65
MoS ₂ - Thermal Decomposition (TD)	0.62

difference of (φ) was observed between structures with thermally decomposed and commercial MoS₂. In addition, commercial WS₂ with lower $\varphi = 0.335$ exhibited higher capacitance 180 mF/cm² compared to capacitance of 116 mF/cm² extracted for commercial MoS₂ with high $\varphi = 0.65$. This suggests that the observed strong increase of the capacitance at low v cannot be correlated with morphology differences between the structures. Further study is required to gain deeper insight into the high su-

percapacitor properties of thermally decomposed MoS₂ and WS₂ disulfides.

3.3 Water splitting electrodes

Thermally decomposed and commercial disulfides were characterized as hydrogen (HER) and oxygen (OER) evolution catalysts for water splitting. Figure 4 (a) shows cyclic voltammetry of electrodes with MoS₂ and electrode with AC measured at dark in 1 M KOH electrolyte. Figure 4(b) shows the same type of electrodes based on commercial and thermally decomposed WS₂ disulfides compared with AC. The current increase of CV at positive voltages is ascribed with OER and at negative voltage with HER. Thermally decomposed MoS₂ and WS₂ disulfides exhibit high hysteresis, which confirms their high capacitance. The catalytic activity for HER and OER reactions can be described by the overpotential required to supply to the system to achieve the selected current density, which is usually 10 mA/cm². The lower overpotential indicates the higher catalytic activity of the selected catalyst. Table 2 summarises the $V_{\text{HER-OP}}$ (for HER) and $V_{\text{OER-OP}}$ (for OER) overpotentials determined

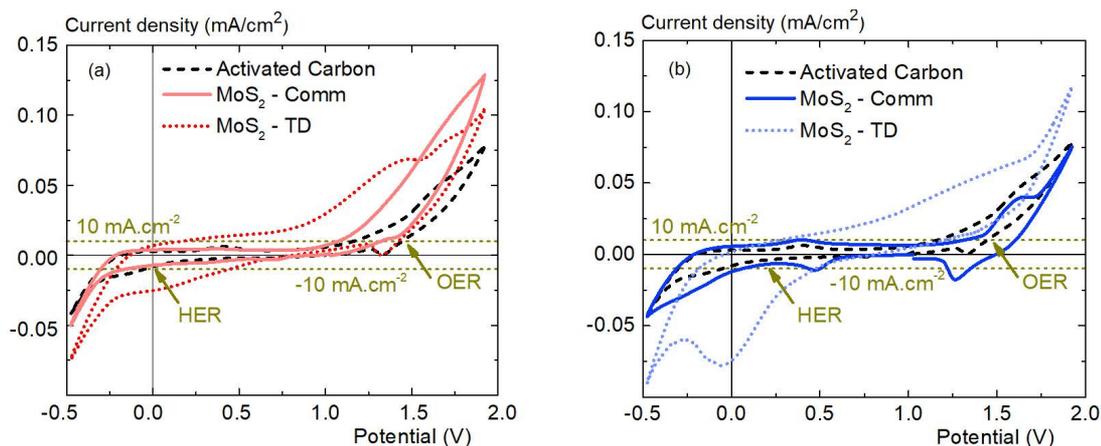


Fig. 4. Cyclic voltammetry of electrodes with: (a) – commercial and thermally decomposed MoS₂ catalysts and AC catalysts, and (b) – commercial and thermally decomposed WS₂ and AC catalysts measured at dark at voltages suitable for hydrogen and oxygen generation

Table 2. Extracted overpotentials at 10mA/cm² from cyclic voltammetry (*V vs RHE*)

Samples	$V_{\text{OER-OP}}$	$V_{\text{HER-OP}}$
Activated Carbon	1.44	-0.30
MoS ₂ - Commercial (Comm)	1.32	-0.30
MoS ₂ - Thermal Decomposition (TD)	1.42	-0.21
WS ₂ - Commercial (Comm)	1.60	-0.31
WS ₂ - Thermal Decomposition (TD)	1.21	-0.18

at 10 mA/cm² from the wider CV curve for studied disulfides and AC electrodes. This wider CV curve was chosen to neglect the impact of hysteresis and different capacitance behaviour. Electrodes with thermally decomposed disulfides exhibit $V_{\text{HER-OP}}$ of 0.21 and 0.18 *V vs RHE* for MoS₂ and WS₂, respectively. These values are lower compared to values obtained on electrodes with commercial disulfides or electrodes with AC. Based on these results, we can ascribe a higher catalytic rate for HER to thermally decomposed disulfides compared to their commercial counterparts or AC-based electrodes. For OER, only thermally decomposed WS₂ exhibits a lower $V_{\text{OER-OP}}$ of 1.21 *V vs RHE* and thus a higher catalytic rate compared to commercial WS₂ and AC. These results confirm the beneficial utilisation of thermally decomposed MoS₂ and WS₂ disulfides for hydrogen generation through water splitting.

4 Conclusions

Presented work describes the preparation and characterisation of the energy conversion and storage structures based on WS₂ and MoS₂ disulfides prepared by thermal decomposition. Obtained results are compared with electrodes prepared from commercially available MoS₂ and WS₂ disulfides. The effect of thermally decomposed disulfides *vs* commercial disulfides on the specific capacitance and hydrogen-oxygen generation was investigated.

Observed hysteresis in cyclic voltammetry curves confirms a capacitive property of prepared supercapacitor structures. Pseudocapacitive charge storage mechanism was indicated by the linear behaviour of the current extracted at $V = -0.4$ V plotted as a function of the square root of the scan-rate. Electrodes with thermally decomposed MoS₂ and WS₂ exhibit high specific capacitance of 405 mF/cm² and 396 mF/cm² at 10 mV/s, respectively. These values are significantly higher compared to 116 mF/cm² and 180 mF/cm² obtained on commercial MoS₂- and WS₂-based electrodes, or 59 mF/cm² obtained on activated carbon electrodes, respectively. The origin of such an increase was discussed in terms of surface area and the presence of micropores.

Thermally decomposed and commercial disulfides were analysed as a catalyst for HER and OER for water splitting. Lower $V_{\text{HER-OP}}$ for both types of thermally decomposed disulfides compared to their commercial counterparts and AC-based structures revealed a higher catalytic rate for hydrogen evolution of prepared MoS₂ and WS₂ materials. The presented study confirmed the perspective utilisation of thermally decomposed disulfides for supercapacitor- and hydrogen generation applications.

Acknowledgements

This work was supported by grants VEGA 1/0529/20, 1/0789/21, and by Ministry of Education, Science, Research and Sport of Slovakia, Slovak Research and Development Agency under the contract APVV-17-0169. The

work was also supported by Program for the Support of Young Researchers by the project SKVEH.

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Received 12 July 2021