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Communication

# Synthesis of vertically aligned porous silica thin films functionalized by silver ions

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**Abstract:** In this work, we have shown the chemical procedure enabling the preparation of the vertically aligned mesoporous silica containing an pre-assumed concentration of the silver ions bonded inside pores via the anchored propyl-carboxyl units. The output materials have been electrochemically verified with regard to the synthesis correctness in order to confirm the efficiency of the fabrication procedure. The mesostructure has been observed using the transmission electron microscope. We have shown, that it is possible to finely tune the functionalization rate during the co-condensation procedure.

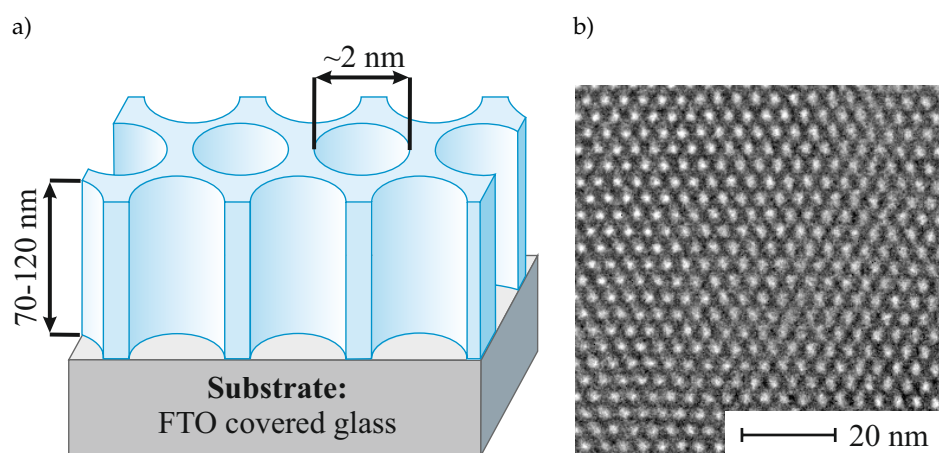
**Keywords:** Mesoporous silica thin films; electro-assisted self-assembly; functional materials.

## 1. Introduction

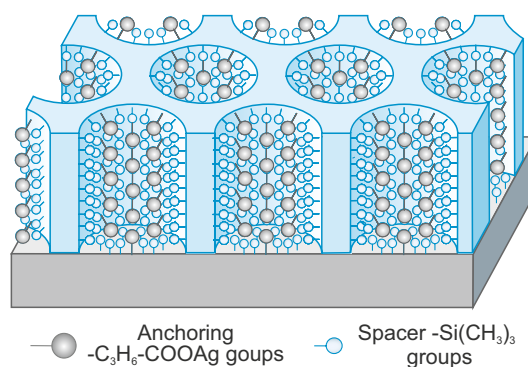
Mesoporous silica thin films build of silicon dioxide (mainly amorphous) are presented in a form of nanometric layers that can be mainly divided into two classes - deposited on various substrates or free-standing [1–4]. These materials have an extraordinary developed surface due to the presence of a vast amount of pores in the structure [5], usually ordered. Depending on the geometry of pores and their mutual location these materials can possess no ordering (have a worm-like structure) or can be 2D structured, 3D cage structured or 3D continuous [6,7]. Moreover, each mentioned type of structure can be divided deeper into numerous subtypes. For example, 2D structured thin films (the most interesting to our group) can possess pores with various diameters, distributed irregularly [8,9] or regularly with possible hexagonal or rectangular arrangement [10–12], laying parallel [13,14] or perpendicular [15] to the surface.

In our opinion, the most interesting from the applicative point of view is 2D regular porous thin films containing vertically aligned mesochannels. Such materials can be used as matrices for the fabrication of functional materials with sophisticated structures accompanying unique properties. The most efficient method for their preparation is the electro-assisted self-assembly method (EASA) resulting in the material containing vertically aligned channels ordered in a 2D hexagonal pattern with a pore diameter of about 2 nm and wall thickness of 1nm [16]. The structure of pristine EASA thin film (non-functionalized) can be seen in 1a along with the transmission electron microscopy (TEM) photography showing the perfect hexagonal arrangement of the pores possible for obtaining by the mentioned method (1b).

Despite their extraordinary structure, the real potential of porous silica thin films became clear after taking into account the possibility of their functionalization [17–20]. From this point of view



**Figure 1.** The structure of a vertically aligned porous silica thin films prepared via electro-assisted self-assembly method (EASA): scheme (a) and TEM microphotography (b)



**Figure 2.** The structure of a vertically aligned porous silica thin films containing silver ions anchored inside pores via propyl-carboxyl units.

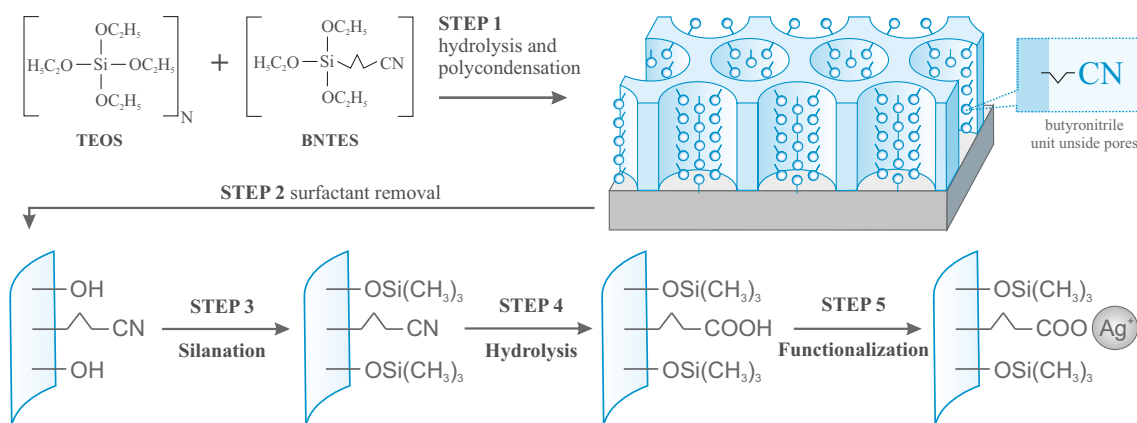
31 vertically aligned mesoporous silica layer can be treated as a unique template, that can be precisely  
 32 modified for particular needs via the deposition of corresponding units (functional groups, molecules,  
 33 nanoparticles, nanowires, etc). Thanks to the extraordinary high specific surface area, such a matrix  
 34 can accommodate a huge number of anchored functional groups on its internal pore surface. What is  
 35 more, we are capable to finely tune their number realizing by it the idea of the "2D solid solvent" [21].

36 In this study, we present the effective procedure allowing for the fabrication of the vertically  
 37 aligned mesoporous silica thin films containing silver ions anchored inside pores via propyl-carboxyl  
 38 units. The structure of assumed material can be seen in fig.2. The number of the silver ions  
 39 accommodated inside pores can be tuned by the variation in the amount of anchoring propyl-carboxyl  
 40 units, incorporated in the silica structure during the co-condensation synthesis procedure. The material  
 41 presented here has great importance as far as antimicrobial layers are concerned. What is more, such  
 42 compounds can be a starting point for the fabrication of the much more sophisticated nanostructured  
 43 composite materials, containing metallic nanowires inside pores (regularly 2D distributed), also the  
 44 multi-layer nanowires (publications in preparation).

## 45 2. Materials and Methods

### 46 2.1. Characterization methods

47 The electrodeposition of silica thin films (chronoamperometry with controlled potential)  
 48 as well as differential pulse anodic stripping voltammetry (DPASV) were carried out using  
 49 potentiostat/galvanostat SP150 (Biologic) at room temperature in the three-electrode configuration.



**Figure 3.** The general procedure of synthesis of vertically aligned mesoporous silica thin films with 2D hexagonally arranged pores containing silver ions inside pores with assumed concentration.

50 The working electrode was a conductive substrate (fluoride-doped tin oxide-covered glass, see next  
 51 section) in the case of electrodeposition of silica thin films, and the same substrate with deposited thin  
 52 films for DPASV measurements. As the counter electrode we used platinum plate, while the reference  
 53 electrode was standard Ag/AgCl. The DPASV measurement was carried out with the 0.1M NaNO<sub>3</sub>  
 54 electrolyte solution. For synthesis and electrochemical measurements we used custom fabricated  
 55 Teflon cell, allowing for the application the substrate at the bottom.

56 The TEM imaging was carried out using the FEI Tecnai G2 20 X-TWIN electron microscope,  
 57 equipped with emission source LaB6 and CCD camera FEI Eagle 2K.

## 58 2.2. Synthesis of vertically aligned mesoporous silica thin films functionalized with silver ions

59 The synthesis of vertically aligned mesoporous silica thin films with 2D hexagonally arranged  
 60 pores containing silver ions inside pores with assumed concentration can be divided on the 5 steps  
 61 summarized in the Figure 3.

62 At the first, the appropriate substrates should be prepared. We used glass plates covered  
 63 pyrolytically by fluoride-doped tin oxide (FTO) conductive layer (purchased at 3D-Nano Ltd). It  
 64 is important to use the pyrolytically layered glass, because only this procedure assures the FTO coating  
 65 strong enough for the harsh reaction involving in the synthesis procedure. As the first, the substrates  
 66 were washed mechanically with the use of detergent. Next, they were washed a few times with DI  
 67 water in the ultrasonic bath following by washing with n-propanol. Finally, FTO glasses were soaked  
 68 in a 1:1 solution of concentrated HCl and ethanol for 15 minutes and washed a few times by DI water  
 69 in the ultrasonic bath. Thoroughly cleaned substrates were dried under the flowing of nitrogen and  
 70 stored under the protective atmosphere.

71 The procedure of electro-generation of functionalized silica thin films (**STEP 1**) starts with  
 72 preparing the mixture containing 20 ml of NaNO<sub>3</sub> (Chempur Ltd) solution in H<sub>2</sub>O (0.1 M), 20 ml of  
 73 ethanol, 0.47 g of CTAB (Merk Ltd) and 4 mmolls of the silica presursors mixture: tetraethylorthosilicate  
 74 (TEOS – Merk Ltd) and 4-(Triethoxysilyl)butyronitrile (BNTES– Merk Ltd). The proportions between  
 75 the two last compounds defines the doping rates of the final materials (the *N* number in the fig. 3).  
 76 In order to yield final molar concentrations of functional units of 10%, 5%, 2.5% and 1.25% (SiO-R  
 77 molecules in all silica-containing molecules) we assumed following proportions TEOS to BNTES: 9:1,  
 78 19:1, 39:1 and 79:1 (*N* numbers of 9, 19, 39 and 79). The mixture were stirred about 15 minutes, till  
 79 CTAB was dissolved. Next, the ph has been decreased to 3 by means of addition of HCl H<sub>2</sub> O (0.1 M).  
 80 The solution was mixed for three hours.

81 The ordered films were received by applying a cathodic potential of 1.5 V for 20 s against the  
 82 Ag/AgCl electrode immersed in a hydrolyzed sol solution. After the thin silica films generation, the

83 electrode surface was immediately rinsed with water and aged overnight at fixed temperature of 130°C  
84 to fix and harden the newly-obtained mesostructure.

85 To extract the surfactant-templated film (**STEP 2**), the samples were dipped into an ethanolic  
86 solution containing 0.1M HCl and maintained under moderate stirring for 15min. After washing a few  
87 times by ethanol, the samples were dried under vacuum for a night.

88 The materials after this stage contain functional butyronitrile (3-cyanopropyl) groups inside open  
89 pores, although silica –OH silanol groups are also presented at the pore surface. The later molecules  
90 can react with carbon at the end of butyronitrile groups during hydrolysis (further step) making  
91 the aimed anchoring units incapable to bonding silver ions. For this reason, we passivated surface  
92 hydroxyl units by silanation (**STEP 3**). To this end, we treat the samples with 2% trimethylsilyl chloride  
93 (TMSCl – Merk Ltd) in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub> – Chempur Ltd). The reaction was carried out in the  
94 Teflon-Parr autoclave at the temperature of 70°C for 24 hours. After this time and cooling down, the  
95 samples were washed a few times with dichloromethane and dried under vacuum at fixed temperature  
96 of 100°C overnight.

97 As-prepared materials were hydrolysed in the next step (**STEP 4**) in order to transform  
98 cyanopropyl group into propyl carboxylic acid units, capable for immobilization of silver ions. To do  
99 this we applied the solution containing concentrated hydrochloric acid (37% – Chempur Ltd) acetone  
100 and water (0.9:0.9:0.2 of volume). The addition of the acetone is a very important in this case, because  
101 pores interior is hydrophobic. Similarly to previous step, also in this case the reaction was done in the  
102 Teflon-Parr autoclave at the increased temperature for 24 hours. After cooling down, the samples were  
103 washed a few times with mixture of water and acetone and dried under vacuum at fixed temperature  
104 of 100°C overnight.

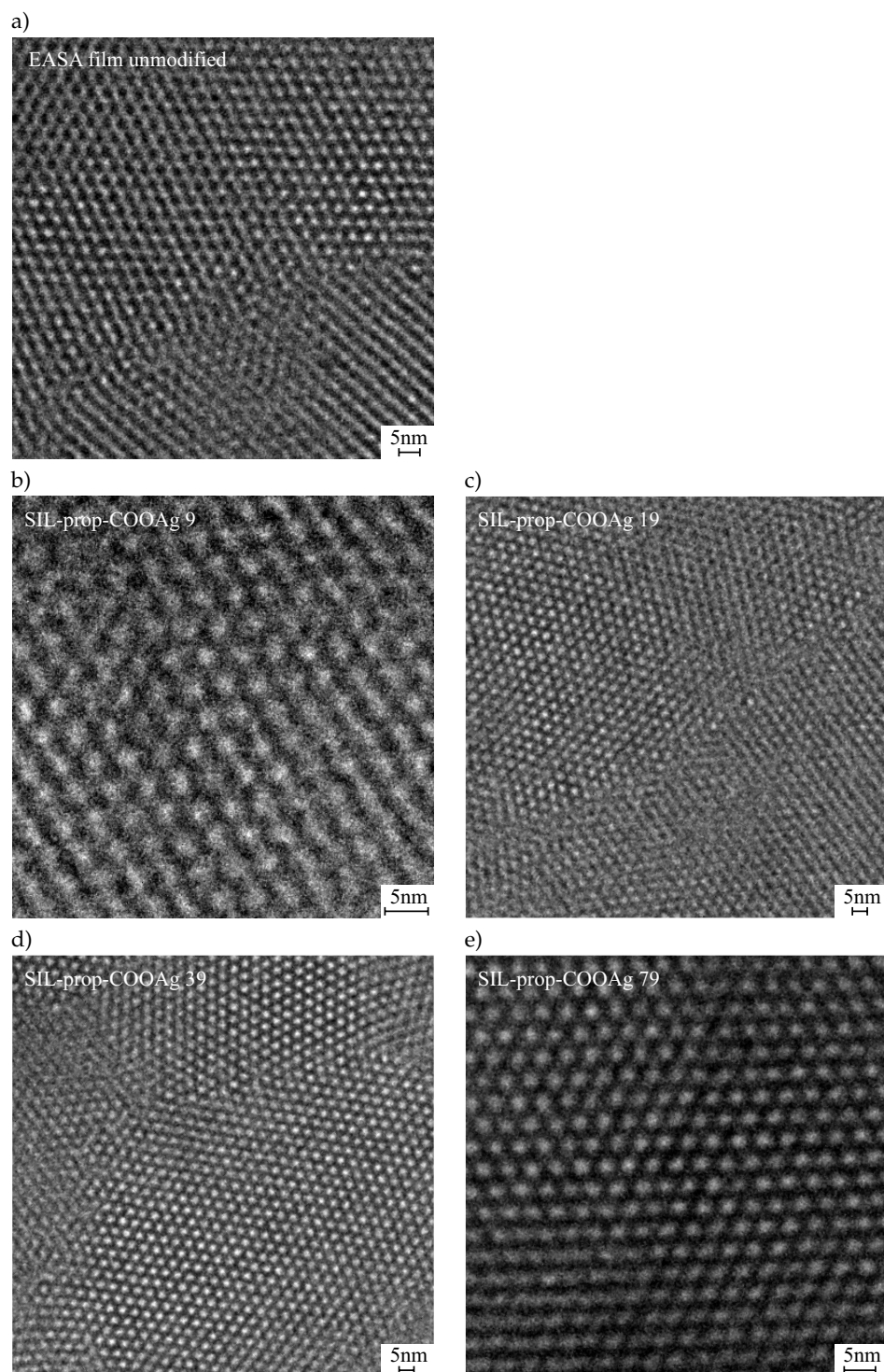
105 At the final step (**STEP 5**), the prepared samples were activated with silver ions. This was done  
106 by interaction of the pre-fictionalized porous silica matrices containing carboxylic acid anchoring  
107 units with the solution of AgNO<sub>3</sub> (Merk Ltd) in water and acetone (1·10<sup>-2</sup> mol/dm<sup>3</sup> in 1:1 mixture of  
108 water and acetone). The reaction procedure was the same, as in previous two steps: under increased  
109 temperature inside Teflon-Parr autoclave. Here we must mention, that all the activities were carried  
110 out in the total darkness, in order to avoid crystallization of the metallic silver in the AgNO<sub>3</sub> solution.  
111 After washing a few times with mixture of water and acetone, and drying, samples were ready.  
112 Obtained materials were stored in total darkness under protective atmosphere of argon.

113 Here it is worthy of mentioning, that the final concentration of silver inside silica channels is  
114 determined by the concentration of the propyl carboxylic acid units: single anchoring groups is capable  
115 for immobilization of the single silver ion, creating silver carbonate molecule. Summing up, we  
116 obtained following samples:

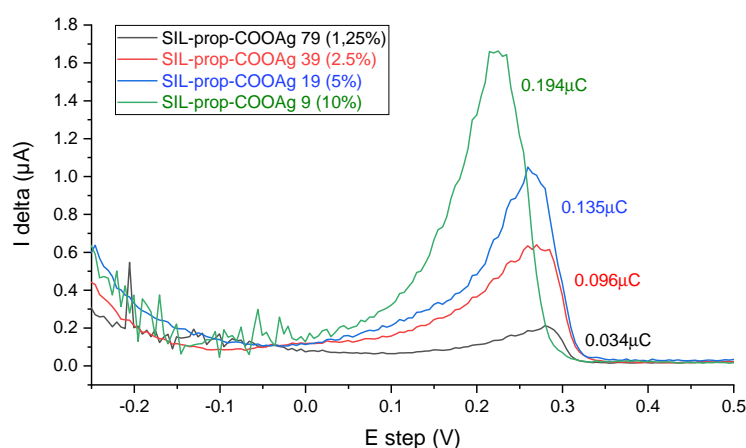
- 117 • vertically aligned porous silica thin films containing 10% of propyl-silver carbonate units inside  
118 pore – 1 OSiR group per 9 SiO<sub>2</sub> – **SIL-prop-COOAg 9**;
- 119 • vertically aligned porous silica thin films containing 5% of propyl-silver carbonate units inside  
120 pore – 1 OSiR group per 19 SiO<sub>2</sub> – **SIL-prop-COOAg 19**;
- 121 • vertically aligned porous silica thin films containing 2.5% of propyl-silver carbonate units inside  
122 pore – 1 OSiR group per 39 SiO<sub>2</sub> – **SIL-prop-COOAg 39**;
- 123 • vertically aligned porous silica thin films containing 1.25% of propyl-silver carbonate units inside  
124 pore – 1 OSiR group per 79 SiO<sub>2</sub> – **SIL-prop-COOAg 79**.

### 125 3. Results and Discussion

126 The first evidence of the obtained materials' correctness was done by means of TEM microscopy.  
127 As it can be seen in Figure 4, all the samples have a correct structure with 2D hexagonal arranged pores,  
128 perpendicular to the substrate. The pores diameter is about 2 nm, while inter-planar distance about  
129 3.5 nm, similar to earlier study [16]. No differences between pure silica thin films and fictionalised  
130 samples can be seen. Also no agglomerations of the doping agent are visible.



**Figure 4.** TEM images of the porous silica thin layers unmodified (a) and containing different concentrations of the functional groups (c–e).



**Figure 5.** Differential pulse anodic stripping voltammetry (DPASV) spectra recorded for silver-functionalized samples: vertically aligned porous silica thin films functionalized by silver ions anchored via propyl-carboxyl units deposited on FTO-covered glass. Samples contain various concentration of the silver carbonate units

The most sensitive technique that is likely to detect even trace amount of the silver ions in the samples is differential pulse anodic stripping voltammetry. Here we must remark, that it is virtually the only method for relative quantification of the silver ions amount. Even X-ray photoelectron spectroscopy (XPS) is not able to detect silver in the vertically aligned porous silica thin films for two reasons: (i) silver-containing specimens have a low photoelectric cross-section and are very hard to detect in small amounts under XPS measurements [22,23] and (ii) porosity of thin films increases the participation of the background signal (the signal originating from the substrate).

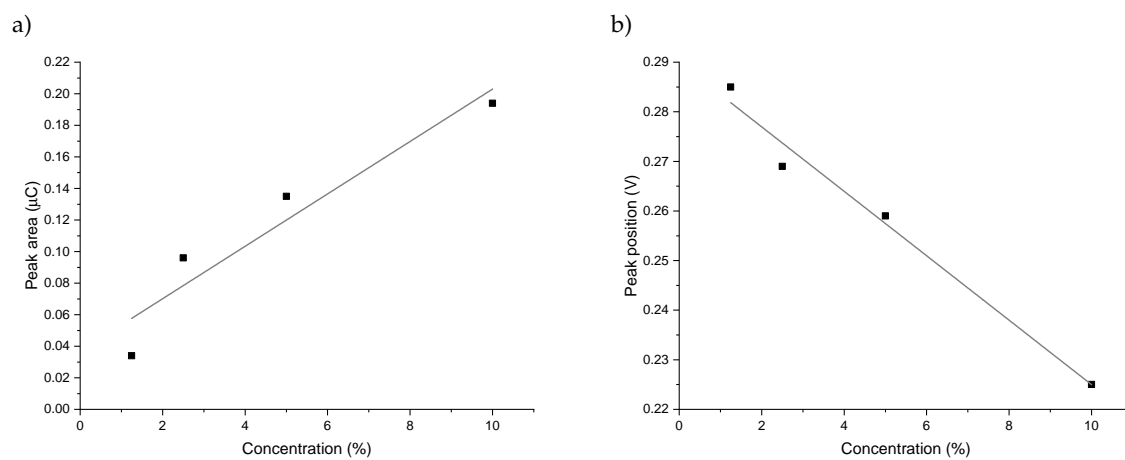
For the reason quoted above, we applied DPASV for the verification of the synthesis procedure by measuring the relative amount of the silver in prepared samples, that was applied as a working electrodes. Since the working solution contained no silver ions all the ions detected via the DPASV scan are related to the ones from the functionalization of the working electrode surface. Typical DPASV results for the samples with different amounts of anchored functional groups can be seen in Figure 5. One can see the presence of peaks for all samples at approximately 0.2-0.3V corresponding the most probably to the silver oxidation. Taking under consideration, that this peak is absent for the non-activated films and their surfaces are directly proportional to the assumed concentration of silver-containing groups (see: Figure 6a), we are convinced of this fact, since the surface area under the DPASV peaks is proportional to the charge transported during the possible oxidation process [24]. What is more, the asymmetric peaks profiles indicating irreversibility of the reaction.

The peaks positions also depend on the concentration of functional groups, as can be seen in Figure 6b. Dear Professor Walcarius, we would be grateful for your help

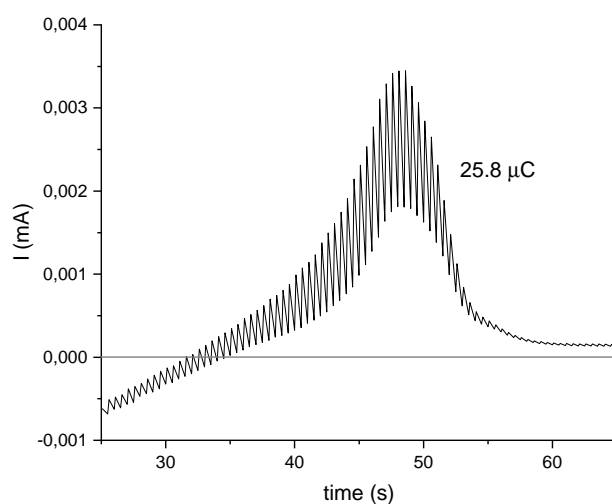
I'm not sure, if the following calculations makes sense...Dear Professor, if you think, that yes, we calculate the ions number also for remaining samples

Plotting the current versus time for the oxidation reaction (during DPASV measurement) (see: Figure.7) and integrating the surface area under the curve one can obtain the charge corresponding to the silver oxidation process. Knowing this value it is possible to estimate the approximate the number of silver ions in one pore. Dividing the charge transferred during oxidation reaction by the elementary charge we are able to obtain the number of electrons involved in the reaction. Assuming Ag(I) configuration of silver in functional units, obtained value is also equal to the number of atoms detected by DPV. In a case of the sample with the highest concentration of silver ions inside pores – sample SIL-prop-COOAg 9 the ions number ( $N_{ions}$ ) can be calculated as follow:

$$N_{ions} = \frac{Q_{el.proc}}{q_{el}} = \frac{25.8 \cdot 10^{-6}C}{1.6 \cdot 10^{-19}C} = 16.1 \cdot 10^{13},$$



**Figure 6.** The dependencies of peaks surface areas (a) and peaks positions (b) on the assumed concentration of the silver in the samples



**Figure 7.** Dependence of current on time during the DPASV measurement for the sample of SIL-prop-COOAg 9 (containing 10% of functional groups) with depicted peak area corresponding to the charge transferred during the electrode reaction



161 where  $Q_{el.proc}$  is the the charge corresponding to process, and  $q_{el}$  is elemental charge.

162 Dividing this number into the number of pores on the electrode surface we will obtain the  
163 approximate minimal number of ions in one pore. The pores density in such kind of thin films is  
164  $7,5 \cdot 10^{12}$  pores per  $1 \text{ cm}^2$  [16].

165 Dear Professor Walcarius, we have recalculated the density of pores. Taking under consideration  
166 hexagonal arrangement and interplannar distance of about 3.5nm, the surface area for single pore is:  
167  $3,5 \times 3,5 \times \sin 60 = 10,6 \text{ nm}^2$ , and this gives  $9,4 \cdot 10^{12}$  pores per  $1 \text{ cm}^2$

168 The surface area of the working electrode was  $0,49 \text{ cm}^2$ , thus the pores number in this area ( $N_{pores}$ )  
169 was  $3,7 \cdot 10^{12}$ . This allows for the calculation the number of ions inside single channel according the  
170 following formula:

$$N_{ions/channel} = \frac{N_{ions}}{N_{pores}} = \frac{16,1 \cdot 10^{13}}{3,7 \cdot 10^{12}} = 43,5 \text{ ions/channel}$$

171 It is worth noticing that this amount of ions in a pore is rather only a minimal amount since it  
172 is unknown if the electrochemical process was fully quantitative and the real number of ions can be  
173 significantly greater. At the same time, obtained here number indicates, that multiple ions can be placed  
174 in one pore and their number can be tuned. In principle, it is possible to tune the average number of  
175 ions in one pore and use them in some in-pore reaction to obtain nanoparticles or nanowires of the  
176 desired size. I'm not sure if we should add this, since this amount is too low to obtain nanocrystals in  
177 the pores. Since we have obtained ones, I assume, that the real number is greater. On the other hand, I  
178 add comments, that it's only a minimal number. Also, we need a discussion. Maybe it is better to do a  
179 separate voltamperogram, but adding one from DPASV we are showing, that it all was done on one  
180 sample

#### 181 4. Conclusions

182 In this work, we have reported a synthesis technique for the fabrication of the vertically aligned  
183 mesoporous silica thin films functionalized by silver ions inside pores. We have shown electrochemical  
184 experiments' results on samples with different concentrations of silver ions inside pores proving, that  
185 calibration of silver ions amount is possible as well as multiple ions could be simultaneously placed  
186 in one pore. Altogether these statements indicate that obtained materials could be used to obtain  
187 nanoparticles or nanowires of the desired size inside pores. Under processing

188 **Supplementary Materials:** The following are available online at [www.mdpi.com/xxx/s1](http://www.mdpi.com/xxx/s1)

189 **Author Contributions:** Conceptualization: AF, LL, ML; data curation: AF, LL; funding acquisition: LL; project  
190 administration: LL; resources: AW, AF, LL, ML, NV, PK; software: KC; supervision: AW, LL, NV; validation: AW;  
191 visualization: AF, LL; writing - original draft: AF, LL, AW, NV; writing - review & editing: AW, AF, LL, ML, NV,  
192 PK, KC.

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196 **Conflicts of Interest:** The authors declare no conflict of interest.

## 197 Abbreviations

198 The following abbreviations are used in this manuscript:

199	EASA	electro-assisted self-assembly
	FTO	Fluoride doped Tin Oxide
	CTAB	cetyltrimethylammonium bromide
200	TEOS	tetraethyl orthosilicate)
	BNTES	butyronitrile triethoxysilane
	TMSCl	trimethylsilyl chloride

## 201 References

- 202 1. Kao, K.C.; Lin, C.H.; Chen, T.Y.; Liu, Y.H.; Mou, C.Y. A general method for growing large area mesoporous  
203 silica thin films on flat substrates with perpendicular nanochannels. *Journal of the American Chemical Society*  
204 **2015**, *137*, 3779–3782.
- 205 2. Yeh, Y.Q.; Lin, H.P.; Tang, C.Y.; Mou, C.Y. Mesoporous silica SBA-15 sheet with perpendicular nanochannels.  
206 *Journal of colloid and interface science* **2011**, *362*, 354–366.
- 207 3. Chen, B.C.; Lin, H.P.; Chao, M.C.; Mou, C.Y.; Tang, C.Y. Mesoporous silica platelets with perpendicular  
208 nanochannels via a ternary surfactant system. *Advanced Materials* **2004**, *16*, 1657–1661.
- 209 4. Laskowski, L.; Laskowska, M.; Jelonkiewicz, J.; Dulski, M.; Wojtyniak, M.; Fitta, M.; Balanda, M. SBA-15  
210 mesoporous silica free-standing thin films containing copper ions bounded via propyl phosphonate  
211 units-preparation and characterization. *Journal of Solid State Chemistry* **2016**, *241*, 143–151.
- 212 5. Mezza, P.; Phalippou, J.; Sempere, R. Sol-gel derived porous silica films. *Journal of non-crystalline solids*  
213 **1999**, *243*, 75–79.
- 214 6. Margolese, D.; Stucky, G.; others. Synthesis of continuous mesoporous silica thin films with  
215 three-dimensional accessible pore structures. *Chemical Communications* **1998**, pp. 2499–2500.
- 216 7. Lee, U.; Kim, M.H.; Kwon, Y.U.; others. Mesoporous thin films with accessible pores from surfaces. *Bulletin*  
217 *of the Korean Chemical Society* **2006**, *27*, 808–816.
- 218 8. Teng, Z.; Zheng, G.; Dou, Y.; Li, W.; Mou, C.Y.; Zhang, X.; Asiri, A.M.; Zhao, D. Highly ordered mesoporous  
219 silica films with perpendicular mesochannels by a simple stöber-solution growth approach. *Angewandte*  
220 *Chemie International Edition* **2012**, *51*, 2173–2177.
- 221 9. Robertson, C.; Beanland, R.; Boden, S.A.; Hector, A.L.; Kashtiban, R.J.; Sloan, J.; Smith, D.C.; Walcarius, A.  
222 Ordered mesoporous silica films with pores oriented perpendicular to a titanium nitride substrate. *Physical*  
223 *Chemistry Chemical Physics* **2015**, *17*, 4763–4770.
- 224 10. Innocenzi, P.; Malfatti, L.; Kidchob, T.; Falcaro, P. Order-Disorder in Self-Assembled Mesostructured Silica  
225 Films: A Concepts Review. *Chemistry of Materials* **2009**, *21*, 2555–2564. doi:10.1021/cm900288x.
- 226 11. Lee, U.H.; Yang, J.H.; ju Lee, H.; Park, J.Y.; Lee, K.R.; Kwon, Y.U. Facile and adaptable synthesis method of  
227 mesostructured silica thin films. *Journal of Materials Chemistry* **2008**, *18*, 1881. doi:10.1039/b718871d.
- 228 12. Klotz, M.; Albouy, P.A.; Ayral, A.; Ménager, C.; Grosso, D.; der Lee, A.V.; Cabuil, V.; Babonneau, F.;  
229 Guizard, C. The True Structure of Hexagonal Mesophase-Templated Silica Films As Revealed by X-ray  
230 Scattering: Effects of Thermal Treatments and of Nanoparticle Seeding. *Chemistry of Materials* **2000**,  
231 *12*, 1721–1728. doi:10.1021/cm991198t.

- 232 13. Bardeau, J.F.; Gourbil, A.; Dutreilh-Colas, M.; Dourdain, S.; Mehdi, A.; Gibaud, A. X-ray reflectivity study  
233 of acid-base post-synthesis treatments of mesoporous thin films templated by {P123}. *Thin Solid Films* **2006**,  
234 *495*, 191 – 196. {EMRS} 2005 Symposium ESynthesis, Characterization and Applications of Mesostructured  
235 Thin Layers, doi:http://dx.doi.org/10.1016/j.tsf.2005.08.357.
- 236 14. Dourdain, S.; Mehdi, A.; Bardeau, J.; Gibaud, A. Determination of porosity of mesoporous silica thin  
237 films by quantitative X-ray reflectivity analysis and {GISAXS}. *Thin Solid Films* **2006**, *495*, 205 – 209.  
238 {EMRS} 2005 Symposium ESynthesis, Characterization and Applications of Mesostructured Thin Layers,  
239 doi:http://dx.doi.org/10.1016/j.tsf.2005.08.356.
- 240 15. Urbanova, V.; Walcarius, A. Vertically-aligned Mesoporous Silica Films. *Zeitschrift für anorganische und*  
241 *allgemeine Chemie* **2013**, *640*, 537–546. doi:10.1002/zaac.201300442.
- 242 16. Walcarius, A.; Sibottier, E.; Etienne, M.; Ghanbaja, J. Electrochemically assisted self-assembly of mesoporous  
243 silica thin films. *Nature materials* **2007**, *6*, 602.
- 244 17. Innocenzi, P.; Malfatti, L. Mesoporous thin films: properties and applications. *Chemical Society Reviews*  
245 **2013**, *42*, 4198. doi:10.1039/c3cs35377j.
- 246 18. jung Chao, K.; hung Liu, P.; ying Huang, K. Thin films of mesoporous silica: characterization and  
247 applications. *Comptes Rendus Chimie* **2005**, *8*, 727–739. doi:10.1016/j.crci.2005.01.004.
- 248 19. Laskowska, M.; Kityk, I.; Dulski, M.; Jędryka, J.; Wojciechowski, A.; Jelonkiewicz, J.; Wojtyniak, M.;  
249 Laskowski, Ł. Functionalized mesoporous silica thin films as a tunable nonlinear optical material. *Nanoscale*  
250 **2017**, *9*, 12110–12123. doi:10.1039/c7nr02786a.
- 251 20. Laskowski, Ł.; Laskowska, M.; Vila, N.; Schabikowski, M.; Walcarius, A. Mesoporous Silica-Based Materials  
252 for Electronics-Oriented Applications. *Molecules* **2019**, *24*, 2395. doi:10.3390/molecules24132395.
- 253 21. Laskowska, M.; Pastukh, O.; Fedorchuk, A.; Schabikowski, M.; Kowalczyk, P.; Zalasiński, M.; Laskowski,  
254 Ł. Nanostructured Silica with Anchoring Units: The 2D Solid Solvent for Molecules and Metal Ions.  
255 *International journal of molecular sciences* **2020**, *21*, 8137.
- 256 22. Chastain, J.; King Jr, R.C. Handbook of X-ray photoelectron spectroscopy. *Perkin-Elmer Corporation* **1992**,  
257 *40*, 221.
- 258 23. Powell, C. Elemental binding energies for X-ray photoelectron spectroscopy. *Applied Surface Science* **1995**,  
259 *89*, 141–149.
- 260 24. Barón-Jaimez, J.; Joya, M.; Barba-Ortega, J. Anodic stripping voltammetry–ASV for determination of heavy  
261 metals. *Journal of Physics: Conference Series*. IOP Publishing, 2013, Vol. 466, p. 012023.