HSA/NANOSILICA BIOCOMPOSITE: STRUCTURAL, TEXTURAL AND MORPHOLOGICAL PROPERTIES

Agnieszka Chrzanowska[1], Ludmyla V. Nosach[2], Ievgenii F. Voronin[2], Anna Deryło-Marczewska[1]

[1]Faculty of Chemistry, Maria Curie-Skłodowska University, pl. Maria Curie-Skłodowskiej 3, 2-031 Lublin, Poland, agnieszka.chrzanowska@poczta.umcs.lublin.pl
[2]Chuiko Institute of Surface Chemistry, NAS of Ukraine, 17 General Naumov Str., Kyiv 03164, Ukraine, info@isc.gov.ua

RESEARCH MATERIAL

New nanoscale silicas and biocomposites based on nanosilica particles and protein molecules are promising materials for biomedical/pharmaceutical applications (eg. enterosorbents and vulnerosorbents). In this work, we prepared new nanosilica supports with unique morphological and textural properties by geometric modification (GM) of initial fumed silica A-300 (nanosilica, Chuiko Institute of Surface Chemistry of NAS of Ukraine) in a specially selected atmosphere using a ball mill [1, 2]. The effectiveness of HSA protein adsorption (Human serum albumin) from aqueous solutions at pH=7.4 on the initial fumed silica (A300) surface and GM-treated nanosilicas (A300-GM) was investigated. The geometrical and textural properties of biocomposite based on fumed nanoscale silica and HSA molecules were characterized using the nitrogen adsorption/desorption isotherms. The micro-nanostructure and morphology of the initial nanoscale silica particles and GM-treated nanosilicas before/after albumin layer adsorption were determined by using the atomic force microscopy (AFM). Additionally, the scanning electron microscopy (SEM) were used to study the topographic properties of the A300 surface support and GM-treated nanosilicas covered by the adsorbed HSA.

NANOSILICA SUPPORT

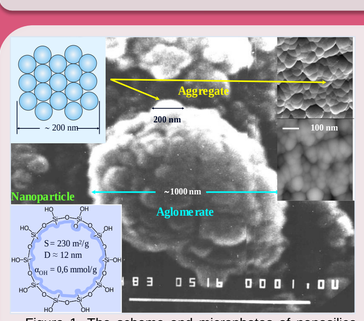

Figure 1. The scheme and microphotos of nanosilica primary particles, aggregates, and agglomerates.

Nanosilics is inorganic, multifunctional enterosorbent with the sizes of primary particles from 10 to 20 nm with pure silica (purity 99.8 %). The initial nanoscale silica possess specific surface area (S_{BET}) ~ 300 m^2/g and bulk density 40-60 g/dm^3 (nanosilica,Chuiko Institute of Surface Chemistry of NAS of Ukraine.

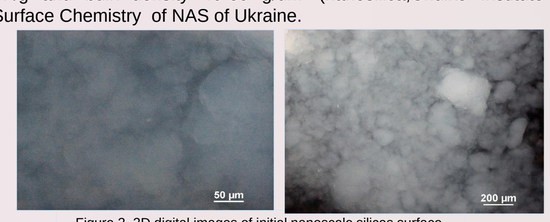

Figure 2. 2D digital images of initial nanoscale silicas surface.

HSA (Human Serum Albumin)

- Molecular weight: 66.439 kDa
- Specific density: 1.36 $g \cdot cm^{-3}$
- Geometrical dimensions, spheroid: 9.5 x 5 x 5 nm
- Geometrical crosssection area: 37 nm^2
- Hydrodynamic diameter: 7 nm

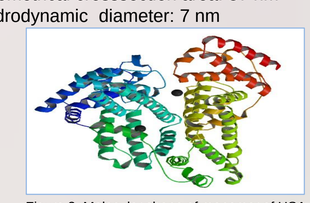

Figure 3. Molecular shape of monomer of HSA (4EMX from RCSB Protein Data Bank).

GEOMETRICAL AND TEXTURAL PROPERTIES - NITROGEN SORPTION RESULTS

NITROGEN ADSORPTION/DESORPTION ISOTERMS

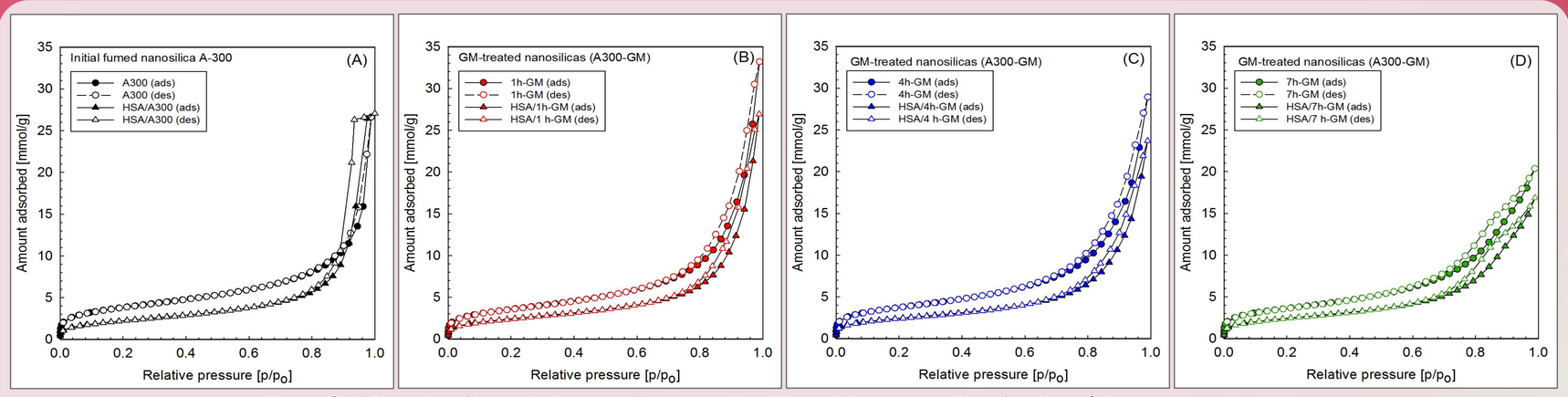

Figure 4. **(A-D)** Comparison of N_2 sorption isotherms of fumed nanosilica A300 and GM-treated nanosilica surface without/with adsorbed protein layer.

STRUCTURE POROUS PARAMITERS

Table 1. The structural characteristics of the initial fumed silica A300 and GM-treated silica materials before/after HSA adsorption calculated from nitrogen adsorption/desorption isotherms .

Sample	[a]t_{GM} [h]	[b]ρ_b [g/dm^3]	[c]S_{BET} [m^2/g]	[d]S_{mic} [m^2/g]	[e]S_{mes} [m^2/g]	[f]S_{mac} [m^2/g]	[g]V_p [cm^3/g]	[h]V_{em} [cm3/g]	[i]V_{mic} [cm^3/g]	[j]V_{mes} [cm^3/g]	[k]V_{mac} [cm^3/g]
Fumed silica A300 and GM nanosilicas											
A300	0	45	301.96	23.17	172.856	105.934	0.923	21.8	0.011	0.341	0.571
1 h-GM	1	191	283.38	15.66	219.772	47.948	1.151	4.8	0.007	0.572	0.572
4 h-GM	4	234	295.60	19.42	232.216	43.964	1.003	3.8	0.009	0.544	0.450
7 h-GM	7	275	286.45	22.92	243.543	19.987	0.706	3.2	0 .011	0.498	0.197
Initial fumed silica A300 and GMA-treated nanosilicas after HSA adsorption											
HSA/A300	-	-	182.47	0	143.347	39.123	0.938	-	0	0.468l	0.470
HSA/1 h-GM	-	-	195.78	0	160.299	35.481	0.932	-	0	0.461	0.471
HSA/4 h-GM	-	-	193.65	5.75	159.328	28.572	0.821	-	0.002	0.425	0.394
HSA/7 h-GM	-	-	195.25	0	180.591	14.66	0.584	-	0	0.417	0.167

[a]t_{GM} mechanical treatment time of silica powder; [b]ρ_b, bulk density of nanosilica samples; [c]S_{BET}, BET specific surface area; [d]S_{mic}, the micropore area; [e]S_{mes}, the mesopore area; [f]S_{mac}, the macropore area; [g]V_t, total pore volume; [h]V_{em}, the empty volume in the powder; [i]V_{mic}, the micropore volume; [j]V_{mes}, the mesopore volume; [k]V_{mes}, the macropore volume.

SURFACE MORPHOLOGY PROPERTIES - ATOMIC FORCE MICROSCOPY

Initial and GM-treated nanosilicas

Initial and GM-treated nanosilicas with adsorber HSA layer

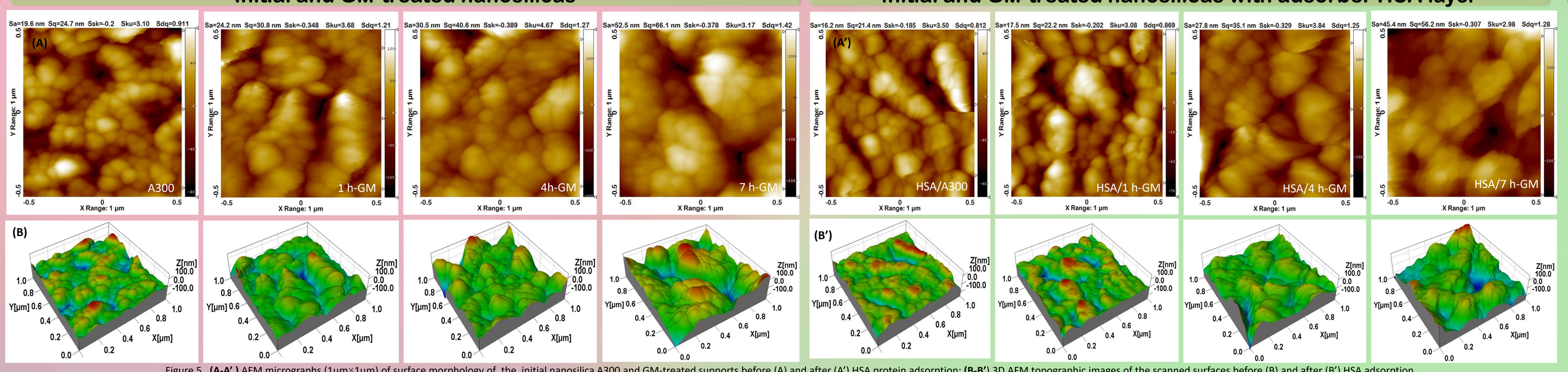

Figure 5. **(A-A')** AFM micrographs (1µm×1µm) of surface morphology of the initial nanosilica A300 and GM-treated supports before (A) and after (A') HSA protein adsorption; **(B-B')** 3D AFM topographic images of the scanned surfaces before (B) and after (B') HSA adsorption.

SURFACE MORPHOLOGY PARAMETERS

Symbol	Name	Description
Sa	Roughness average	arithmetic mean of the absolute height value
Sq	RMS surface roughness	standard deviation of the profile heights values
Sdq	RMS slopes –surface waviness	RMS value of the surface slope
Ssk	Surface skewness	height distribution asymmetry
Sku	Surface kurtosis	height distribution sharpness (peakedness)

Sample	S_a [nm]	S_q [nm]	S_{dq} [rad]	S_{sk}	S_{ku}
A300	19.6	24.7	0.91	-0.200	3.10
HSA/A300	16.2	21.4	0.81	-0.185	3.50
1 h-GM	24.2	30.8	1.21	-0.348	3.68
HSA/1 h-GM	17.5	22.2	0.87	-0.202	3.08
4 h-GM	30.5	40.6	1.27	-0.389	4.67
HSA/4 h-GM	27.8	35.1	1.25	-0.329	3.84
7 h-GM	52.5	66.1	1.42	-0.378	3.17
HSA/7 h-GM	45.4	56.2	1.28	-0.307	2.98

Table 2. Parameters characterizing the surface morphology of initail silica A300 and GM- treated nanosilica suports before/after protein adsorption.

SURFACE TOPOGRAPHY ANALYSIS - SCANNING ELECTRON MICROSCOPY

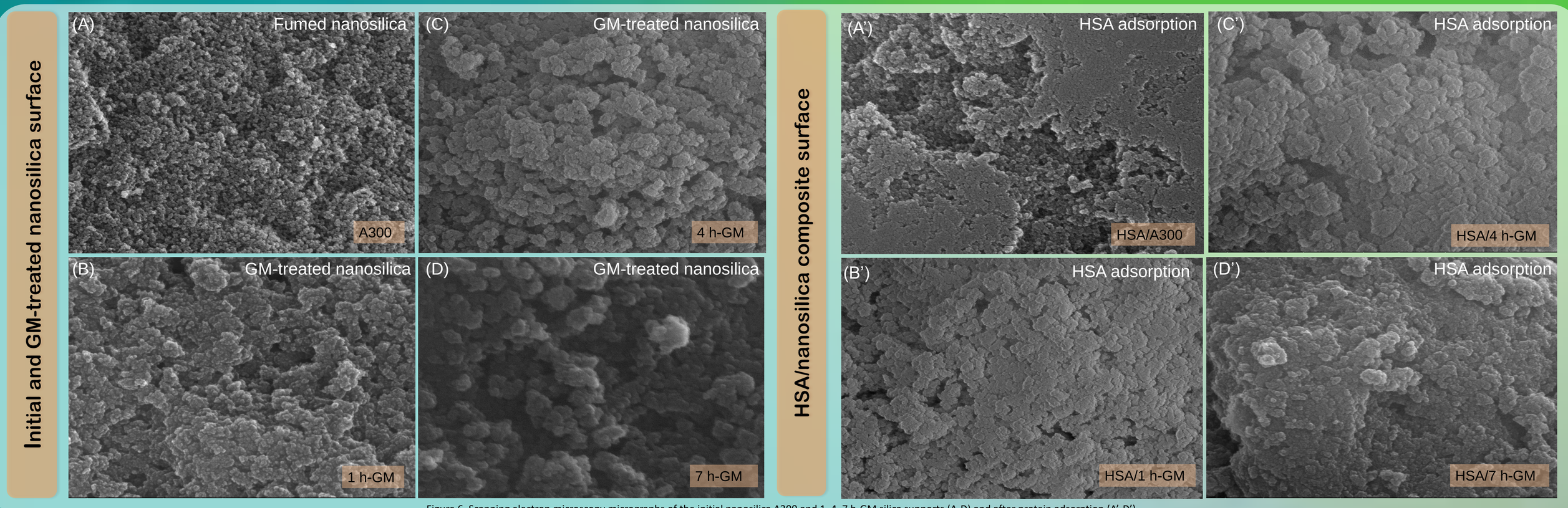

Figure 6. Scanning electron microscopy micrographs of the initial nanosilica A300 and 1, 4, 7 h-GM silica supports (A-D) and after protein adsorption (A'-D').

CONCLUSIONS

- HSA protein adsorption capacity of the nanosilica support is systematically diminishes with increasing mechanical treatment time of nanosilica supports.
- Analysis of porous structureof the initial silica A300 and GM-treated samples by means of the low temperature nitrogen adsorption/desorption showed that the parameters of porous structure *(S_{BET}, S_{ext}, V_t, D_{av}, D_{hy})* after adsorption of HSA albumin are reduced.
- AFM analysis showed that the morphology and microstructure of the initial and GM-treated nanosilicas surface with the adsorbed proteins molecules are less porous than the surface of the initial silica material and 1, 4, 7 h-GM silica supports. The surface roughness *(S_q)* and waviness *(S_{dq})* decreases after protein adsorption on the adsorbent surface.
- SEM analysis witn/without protein adsorption layer confirm the structure and presence of the adsorbed albumin molecules on the nanosilica surface.
- GM- treatment conditions (t_{GM}) of the silica supports make changes the surface topography and textural properties (grain/particle sizes) of material to a larger extent than the unmodified A300 fumed silica.

REFERENCES:

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