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# Microbead Silica Decorated with Polyhedral Silver Nanoparticles as a Versatile Component of Sacrificial Gel Films for SERS Applications

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A new method of microbead silica preparation with superficially built-in 2-3 nm silver seeds is suggested by using a simple reaction of Stoeber SiO<sub>2</sub> microspheres with hot aqeuos solutions of diamminesilver (I) hydroxide without addition of reducing agents. The seeding beads initiate growth of polyhedral 20 - 50 nm silver nanopartices encrusting silica surface after an instant heterogeneous contact with a mixture of silver nitrate and ascorbic acid solutions with concentrations of as low as 1 mM. The unique microstructure results in a pronounced, about 100 nm, red shift of the silver plasmonic band allowing fast and robust tuning of optical properties of the nanocomposites. Such microengineered building blocks are stored safely in a sacrificial biopolymer (ethylcellulose) film as its versatile component to be applied on demand in aqueous environment since polymer swelling absorbs water - soluble analytes and allows for the advanced SERS analysis.

#### Starting time adjustment for silver nanoparticle growth

Silver ammonia complex was heated and kept at 90<sup>o</sup>C for 10, 20 and 30 minutes. After the solution has become weakly yellow-coloured, about 0,3 g of dried silica was added and stirred in the solutions. After 30 minutes, the reaction was stopped and the precipitate was cleaned with Mill-Q and redispergate in water. The yellow powder was saved as seeds.

#### Repeated growth

The seeding silver - silica microspheres were added into silver complex of different concentrations and kept for different time (Table S1, Fig.S1). The estimates of silver content within 6 - 14% with respect to Si (Table S1) demonstrate that it does not depend much on either initial concentration of the silver complex or soaking time probably because of a balance of silver seed formation dynamics and surface etching process kinetics of silica with a base solution

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of the complex which generates more OH- ions with respect to aqueous  $NH_3$ . Thus the only one concentration and the only one time was selected to obtain seeding microspheres as described in the Experimental part of the paper.



**Fig.S1.** Samples repeatedly treated in a hot solution of ammonia complex of silver (I) oxide after formation of seeding silica beads (see Table 1).

Table.S1.	Numberii	ng of	repeatedly	treated	seeding	silica
beads <sup>*</sup> in	hot (90 -	95 <sup>0</sup> C) :	solution of t	he ammo	nia comp	lex of
silver (I) o	xide of dif	ferent	concentratio	ons, (see	Fig.S1)	

Time, min $\rightarrow$	10	20	60
Concentration,			
м↓			
0.01	1**	4	7****
0.005	2	5	8
0.001	3***	6	9****

The Si:Ag ratio according to EDX: \*6.7:1, \*\*15.1:1, \*\*\*6.3:1, \*\*\*\*15:1, \*\*\*\*6.8:1.

## ARTICLE

#### Injection method

As-prepared silver ammonia 0.01M complex and Stoeber microspheres were mixed together in a weight ratio of about 10:1 and 5 ml of the mixture was injected into 50 ml of boiling water. After 30 minutes, the reaction was stopped and the precipitate was cleaned with Mill-Q water and redispergate (Fig.S2).



**Fig.S2.** Silica - silver composite SEM microstructure. a. Injection of Stoeber silica beads within the aliquot of ammonia silver complex (0.01M) into boiling water, etching of the surface is obvious, the inset shows EDX spectra of the sample with no impurities. b. Self – assembling of silver – silica microspheres.

The given images evidence for silica surface etching, the presence of pure silver and the possibility of self - assembling of the microspheres in photonic-crystal-like structures. All the samples contained small particles of metallic silver without impurites like silver (I) oxide as evident from the XRD data in Fig.S3.

A comparison of the new ammonia – derived seeding technique with traditional seeding approaches is given in Fig.S4 – S5. It is evident (Fig.S5) that the new seeding procedure provides a quite uniform distribution of 2-5 nm silver seeds over the superficial layer of silica and it is achieved in one simple and inexpensive stage of an interaction with a hot ammonia solution.



**Fig.S3.** A magnified part of a typical XRD pattern of silica seeding sample with moderate broadening of XRD peaks.

 $NaBH_4$  as a strong reducing agent provides often free silver nanoparticles detached from the surface of silica (Fig.S5,b) and it results in uniform silver seeds if the surface contains intensially incorporated aminogroups for an electrostatic interaction with silver nanoparticles (Fig.S5,c).



**Fig.S4.** Forcing aggregation of traditional  $Ag@SiO_2$ microspheres (prepared by the reduction of  $AgNO_3$  solution with  $NaBH_4$ ) by an addition of  $10^{-4}M$  cysteamine in their suspension in water. Note that silver nanoparticles are located between the microspheres mostly and the microspheres form large aggregates.

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**Fig.S5.** Comparison of traditional seeding schemes with the developed ammonia – derived seeding procedure. a. uniform distribution of small silver seeds in the superficial layer of silica microspheres in the case of an application of the new seeding technique suggested in this work that utilizes hot ammonia solutions, b. silver nitrate reduction by NaBH<sub>4</sub> in the presence of bare silica microspheres, note large aggregates of free silver nanoparticles detached from the surface of silica and the absence of uniformity of silver nanoparticle distribution, c., d. secondary electron and back – scattered images of a Ag@SiO<sub>2</sub> nanocomposite prepared using the same traditional procedure of silver nitrate reduction by NaBH<sub>4</sub> in the presence of silica microspheres covered preliminary by an  $NH_2$  – group containing layer of silica as achieved by introducing of an additional expensive and time – consuming stage of (3 - aminopropyl)triethoxysilane hydrolysis, note an increase of the microsphere diameters and more uniform distribution of attached silver nanoparticles.



**Fig.S6.** Different view angles under direct sun light for a glassy vial with diluted  $Ag@SiO_2$  nanocomposite suggested in the present work, the solution is stable at least 3 - 4 days at room temperature forming no precipitates, a. background illumination, b. side view, c. front view.



**Fig.S7.** The very first stage of polymer –  $Ag@SiO_2$  film preparation onto embossed aluminum foil using droplets of  $Ag@SiO_2$  suspension in 0.5wt % solution of ethylcellulose, a, b, c - suspensions with an increasing ratio of  $Ag@SiO_2$  and ethylcellulose, 1 - as - prepared "green" suspension droplets for a further SERS analysis, 2 - empty embossed cells in the aluminum foil. The same color as in Fig.S6 is observed.

**Fig.S8.** A film of polymer  $-Ag@SiO_2$  xerogel inside embossed aluminum foil cells after drying the samples in Fig.S7 at room temperature, the cells are ready for a SERS analysis of different analytes. The same phenomenon of color change depending on a view angle, as in Fig.6, is observed. a, b, c - flash light directed from above perpendicular to the samples with an increasing ratio of  $Ag@SiO_2$  and ethylcellulose. d. side illumination. These multiple cells are easy to produce at a laboratory scale.



**Fig.S9.** An alternative preparation way of SERS substrates with multiple cells after  $Ag@SiO_2$  - ethylcellulose gel drying at room temperature over the whole substrate, 1 - aluminum foil, 2 -  $Ag@SiO_2$  - ethylcellulose film in the embossed cells, b - a cut piece (2) of the substrate stored in a glassy vial (1) with free - standing film pieces on the bottom (3).



**Fig.S10.** Visual stages of  $Ag@SiO_2 - polymer swelling$ , a macrophoto view. a. an initial 4\*4 mm thick piece of the  $Ag@SiO_2 - ethylcellulose xerogel$ , b. an excessive droplet of liquid (water in this particular case) is added, c. water penetration in the gel structure with its volume increase due to swelling, d. the final stage of swelling.

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An application of ethylcellulose makes it easy to prepare SERS - active substrates over a large area (Fig.S6 - S9). Ag@SiO<sub>2</sub> consumption remains low, estimates gives less than 1 mg of silver per square centimetre of the substrate. The film is more uniform in the case of gel casting over the whole area of a chosen substrate (Fig.S9, a) while casting of the gel containing silver - silica nanocomposite into separate embossed cells (Fig.S8) gives a possibility to vary properties of each cell separately, for example, a change of the ratio of Ag@SiO<sub>2</sub> and ethylcellulose could lead to an interplay with the film thickness, adhesion to the substrate and the number of SERS - active centers. Each cell is suitable for a measurement of one analyte while the whole substrate with multiple cells allows for a SERS analysis of several different series of analytes. The substrate with such a SERS active layer can be cut into pieces, that could be stored under different conditions, can uptake, hypothetically, gaseous analytes inside hermetic vessels (Fig.S9,b) etc. In the case of liquid analytes, the polymer swelling phenomenon (Fig.S10) results in preconcentrating of analytes from an added volume of the liquid into the bulky layer of the swelled gel with the spatially distributed SERS nanocomposite. Thus, the suggested approach allows to advance preparation procedures of SERS substrates with desired properties.



**Fig.S11.** DLS data for the  $Ag@SiO_2$  nanocomposite in water (1) and the same with 0.5 wt% of ethylcellulose added (2). The numbers note zeta - potentials of the  $Ag@SiO_2$  microspheres.

Another positive influence of ethylcellulose is shown in Fig.S11. It seems that the polymer forces  $Ag@SiO_2$  microspheres to aggregate partly which could enhance a SERS signal due to possible hot spots in the aggregates.