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Silver nanoprisms self-assembly on differently functionalized silica surface

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Abstract. In this work colloidal silica/silver nanoprisms (NPRs) composite coatings were made. Firstly colloidal silica sols were synthesized by sol-gel method and produced coatings on glass by dip-coating technique. Next coatings were silanized by (3-Aminopropyl)triethoxysilane (APTES), N-[3-(Trimethoxysilyl)propyl]ethylenediamine (AEAPTMS), (3-Mercaptopropyl)trimethoxysilane (MPTMS). Silver NPRs were synthesized via seed-mediated method and high yield of 94 ± 15 nm average edge length silver NPRs were obtained with surface plasmon resonance peak at 921 nm. Silica-Silver NPRs composite coatings obtained by self-assembly on silica coated-functionalized surface. In order to find the most appropriate silanization way for Silver NPRs self-assembly, the composite coatings were characterized by scanning electron microscopy (SEM), dynamic light scattering (DLS), water contact angle (CA) and surface free energy (SFE) methods. Results have showed that surface functionalization is necessary to achieve self-assembled Ag NPRs layer. MPTMS silanized coatings resulted sparse distribution of Ag NPRs. Most homogeneous, even distribution composite coatings obtained on APTES functionalized silica coatings, while AEAPTMS induced strong aggregation of Silver NPRs.

1. Introduction

Noble metal nanoparticles have been investigated and applied in many research areas including chemical catalysis [1], biochemistry [2, 3], optics [4-6], and electronics [7]. Currently, scientists are focused on anisotropic Silver and Gold nanoparticles properties and their application in various fields [8-10]. There are many references about synthesized silver and gold nanocubes [11], nanododecahedron [12], nanodiscs [13] and nanoprisms [9]. Silver nanoprisms (NPRs) are one of the most interesting nanoparticle type, because of wide tuneability and high intensity of surface plasmon resonance (SPR) band [14, 15]. Manipulating particle thickness and edge length, it is possible to obtain SPR peak position in 400 – 1300 nm range, when conventional spherical particles can only exceed up to 600 nm [16]. These properties opens the gateway for application in near infrared working technologies, like telecommunications [16] or surface enhanced Raman spectroscopy (SERS) [17].

Our research is focused on synthesis of Silver nanoprism composite materials. One of the approaches are silica/Ag NPRs coatings. Currently many papers are available on production various types of composites with Ag NPRs. Most of them are about integration those particles to different polymer matrices [18, 19], but still lacking references on use of inorganic matrix. Our selected way is make silica-silver nanoprism coatings by self-assembly of particles on silanized silica surface. Xue, C.,



et al. [20, 21] already did some research on this topic. However, information about how different surface affects Ag NPRs self-assembly are still missing.

In this work we investigated how differently prepared silica surface affects assembly of silver NPRs. Therefore we synthesized a Silver NPRs with average edge lengths of 94 ± 15 nm, made silica coatings by sol-gel technique, silanized surfaces using different APTES, AEAPTMS MPTMS, and deposited NPRs on silanized surface. Produced composite coatings were evaluated by scanning electron microscopy (SEM) and UV-VIS spectroscopy.

2. Experimental

2.1. Chemicals and Materials

Tetraethyl orthosilicate (TEOS, 98%), (3-Aminopropyl)triethoxysilane (APTES, 99%), N-[3-(Trimethoxysilyl)propyl]ethylenediamine (AEAPTMS, 98%), (3-Mercaptopropyl)trimethoxysilane (MPTMS 99%), Silver nitrate (AgNO_3 , 99%), Poly(sodium 4-styrenesulfonate) (PSSS, 1000000 Mw), Sodium Borohydride (NaBH_4 , 99%), L-Ascorbic Acid ($\text{C}_6\text{H}_8\text{O}_6$, 99%) were purchased from Sigma-Aldrich and used without further purification. Absolute ethanol (99.9 %) prepared by refluxing with preheated CaO, and after distilled.

2.2. Synthesis of silver NPRs.

Silver NPRs were made by seed-mediated method which include two steps – producing silver nanoseeds and nanoprism growing.

Making silver seeds. In this experiment, silver seed are obtained by mixing aqueous trisodium citrate (20 mL, 25 mM), PSSS (1 ml, 0.5 g/L), freshly prepared NaBH_4 (1.2 mL, 10 mM) solutions, followed by addition of aqueous AgNO_3 (20 mL, 0.5 mM). Addition rate of AgNO_3 was 2 mL/min. The rate was maintained using syringe pump.

Growing of NPRs. Silver NPRs are produced by mixing 35 ml distilled water, aqueous ascorbic acid (0.525 mL, 10 mM) solution, 0.560 mL of prepared silver seeds solution, followed by addition of aqueous AgNO_3 (21 mL, 0.5 mM) at a rate of 1 mL/min. Obtained Silver seeds and NPRs solutions characterized by UV-VIS spectroscopy (Perkin Elmer Lambda 35), Scanning Electron Microscopy (SEM, Hitachi FE-SEM SU-70).

2.3. Synthesis of colloidal silica and coating procedure

Colloidal silica sols in ethanol were made by base catalyzed TEOS hydrolysis and condensation. For that purpose TEOS, Ammonia, Water, and Ethanol were mixed with molar ratio 1:0.2:2.3:38 respectively. Sols were left at room temperature for 10 days. Particle size was determined by Dynamic Light Scattering (DLS, Malvern Instruments Zetasizer Nano ZS) method.

For coating process microscope soda-lime glass slides were used as substrate. Substrates were cleaned by immersing them in piranha solution (volume ratio 1:4 of H_2O_2 and H_2SO_4 respectively) for 15 min. Then substrates were washed with deionized water few times, and dried by leaving in desiccator for 24 h at room temperature. Coatings were made by Dip-Coating technique (KSV Dip Coater D). For all samples were used constant 40 mm/min withdrawal speed. Coated samples were ready for the next step – surface silanization.

2.4. Surface silanization and deposition of Silver NPRs.

Thermal silanization. Coatings and uncoated substrates were functionalized by alkoxysilanes – APTES, AEAPTMS and MPTMS. Same silanization procedure were used for all silanes. In first step three different 3% alkoxysilane solutions in toluene were prepared. Then substrates were immersed in prepared solution and refluxed for 12 hours under argon atmosphere. After silanization procedure, substrates were washed several times with pure toluene and acetone.

For deposition of Silver NPRs, functionalized substrates were immersed in previously prepared Silver NPRs colloidal solution and kept for 7 days. The composite coatings were gently washed with distilled water and left to dry in room temperature.

3. Results and discussions

3.1. Synthesis of Silver NPRs

For silver nanoprism synthesis was selected the seed-mediated method, which was previously suggested by Aherne, D., et al. [14]. Synthesized particles by this method are sufficiently monodisperse, and comparing with photoconversion method [22] is performed faster and easier.

In synthesis method Sodium citrate and PSSS were used as particle shape determining materials. Silver NPRs were synthesized in high yield, with edge length about 94 ± 15 nm. Average particle sizes were calculated from SEM micrographs (fig 1.) As can be seen from fig. 1, obtained particles are plate-like structure and almost all have trigonal or hexagonal shape, but varies in size. Particle shape and size plays significant role in their optical properties. SPR band of high aspect ratio Ag particles (plate-like structures) like nanoprisms, nanohexagons or nanodiscs generally are in longer wavelengths (700-1200 nm). Higher aspect ratio of particle gives red-shifting of SPR band. In case of Silver nanoprisms, significant role plays tip length of the prism – sharper prisms give more red-shifted SPR band, and duller – blue-shifted. Therefore nanohexagons also can be considered as prisms having dull tips.

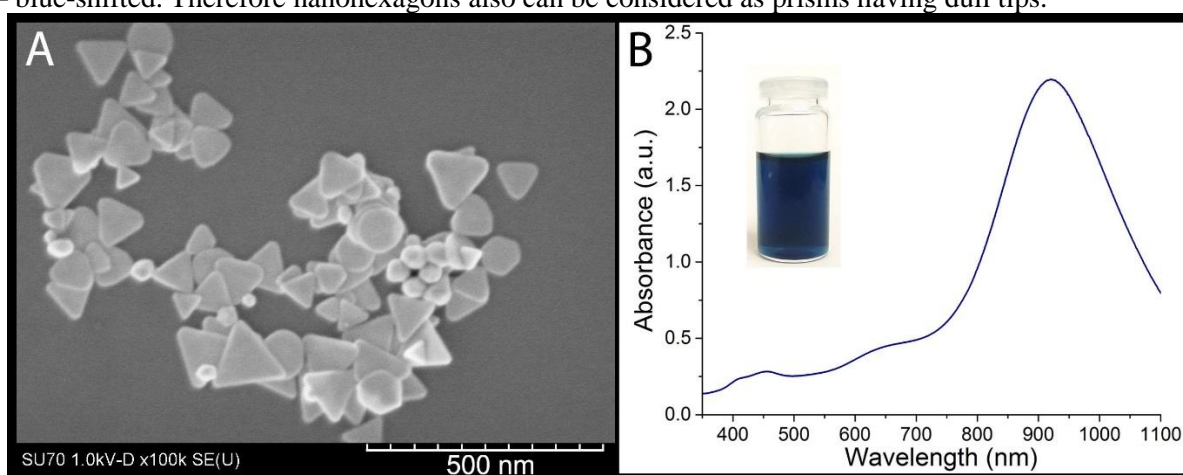


Figure 1. SEM images of synthesized Ag NPRs particles (A) and absorption spectra of synthesized Ag NPRs solution (B)

Obtained colloidal Silver NPRs solution are relatively stable and no significant changes were observed in few months. Single SPR band (fig. 1) shows high intensity absorption at 921 nm, which gives a blue color of NPRs colloidal solution. Red-shifted SPR peak indicates presence of high aspect ratio anisotropic particles like triangular NPRs in solution. SPR peak is slightly broadened, but it is common for all plasmonic particles which has absorption in near infrared [8].

3.2. Synthesis of colloidal silica, fabrication of coatings and surface silanization

As mentioned in experimental section, in this research base catalyzed silica sol were used. During this reaction, usually forms silica spheres which diameter can be varied from nanometer to submicrometer scale. Exact size of the spheres is controlled by initial ratio of starting materials [23]. Accordingly, 3% (w/w) monodisperse colloidal silica in ethanol, with 30 ± 11 nm average sphere diameter were made by selecting appropriate ratio of standing materials [24]. After sol synthesis, coatings were formed using dip-coating method and samples were kept for next step – surface functionalization.

In this work we selected thermal silanization method. By this technique, ideally, only one layer of silane is formed on coating surface. Coated substrates functionalized by – APTES, AEAPTMS and MPDMS. Coatings made of 20-30 nm silica particles have higher surface area and more hydroxyl groups comparing with activated bare glass surface which leads to higher amount of attached silane molecules during silanization procedure. This surface silanization method is well-studied, however silanized surface must be characterized to make sure, that surface functionalization were succeeded. In our case,

to make sure that silanization process was successful, water contact angles (CA) and surface free energy (SFE) measurements were made (table 1).

Table 1. Measured water contact angle and SFE values of silanized coatings

Sample name	Modifying silane	Contact angle, deg.	Dispersive free energy, mN/m	Polar Surface free energy, mN/m	Total Surface free energy, mN/m
JV011	None	40.20	36.80	24.27	61.07 ±4,45
JVm1	APTES	69.75	31.16	9.82	40.98 ±5,09
JVm2	AEAPTMS	66.75	25.94	13.55	39.48 ±4,60
JVm3	MPTMS	54.84	37.55	14.94	52.49 ±5,31

For SFE measurements we selected Harmonic Mean (Wu) method which gives more accurate results when surface have high SFE values. In order to calculate surface free energy, in contact angle measurements we used four solvents – diiodomethane, water, glycerol and ethylene Glycol.

As can be seen form table 1, all silanized coatings have higher CA and smaller total SFE values, comparing with non-silanized coating. As result of high amount of polar hydroxyl groups on surface, highest wetting properties have non-functionalized silica films. Due to polar amine groups, APTES and AEAPTMS silanized coatings must give better wetting properties, but grafted carbon chain can give higher water contact angle value and smaller surface free energy values. MPTMS modified coatings has slightly better wetting properties and higher surface free energy comparing with APTES and AEAPTMS functionalized coatings.

3.3. Silver NPRs self-assembly on silanized surfaces

In this section we investigated silver NPRs self-assembly on differently silanized silica coatings. We tried to find out which silanized surface is more suitable for assembly of NPRs. Thus, as mentioned in experimental section, in order to obtain self-assembled silver NPRs layer, functionalized coatings were vertically immersed in plastic vials with containing silver NPRs solution and kept for 1 week at room temperature. After this procedure, samples were ready for UV-Vis measurements.

Firstly, we took pictures of samples (fig. 2) to visually evaluate how silver NPRs assembled on silanized silica coatings.

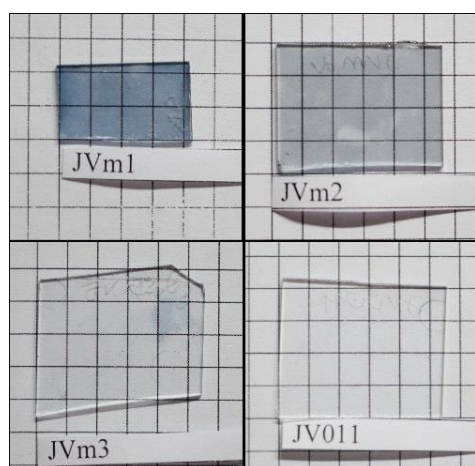


Figure 2. Images of Ag-silica composite coatings

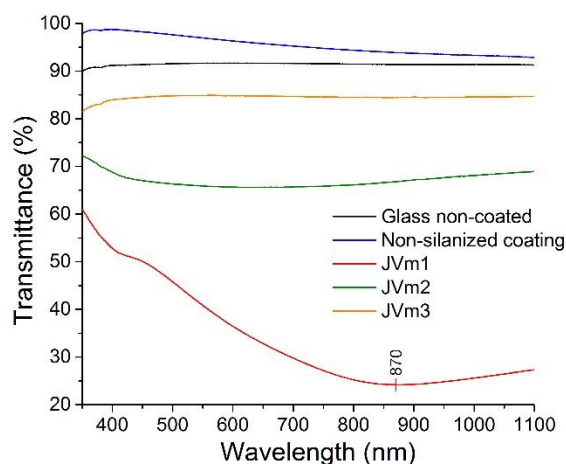


Figure 3. Transmittance spectra of Ag-silica composite coatings

On APTES silanized coating layer of assembled Ag nanoparticles is clearly visible. The latter layer gives intensive blue color. In UV-Vis (fig. 3) transmittance spectra's is visible strong absorbance around 870 nm in case of APTES functionalized coating. Also are noticeable, that this SPR peak is broadened and blue shifted comparing with the Ag NPRs solution. This may be caused by change of surrounding media of the particle – dielectric environment and refractive index of surrounding affects position of SPR [25]. In case of AEAPTMS functionalized coatings, Ag nanoparticles layer become

blue-greyish. It can be result of large amount of primary and secondary amine groups, which may induce stronger attraction and later agglomeration of Ag nanoparticles. Thus, no SPR peak, only broad absorbance are visible in UV-Vis spectra of this sample. Ag NPRs layer is barely visible on MPTMS modified and unmodified coatings.

In addition coatings were investigated by SEM. SEM images of differently silanized-Ag NPRs self-assembled coatings are presented in figure 4.

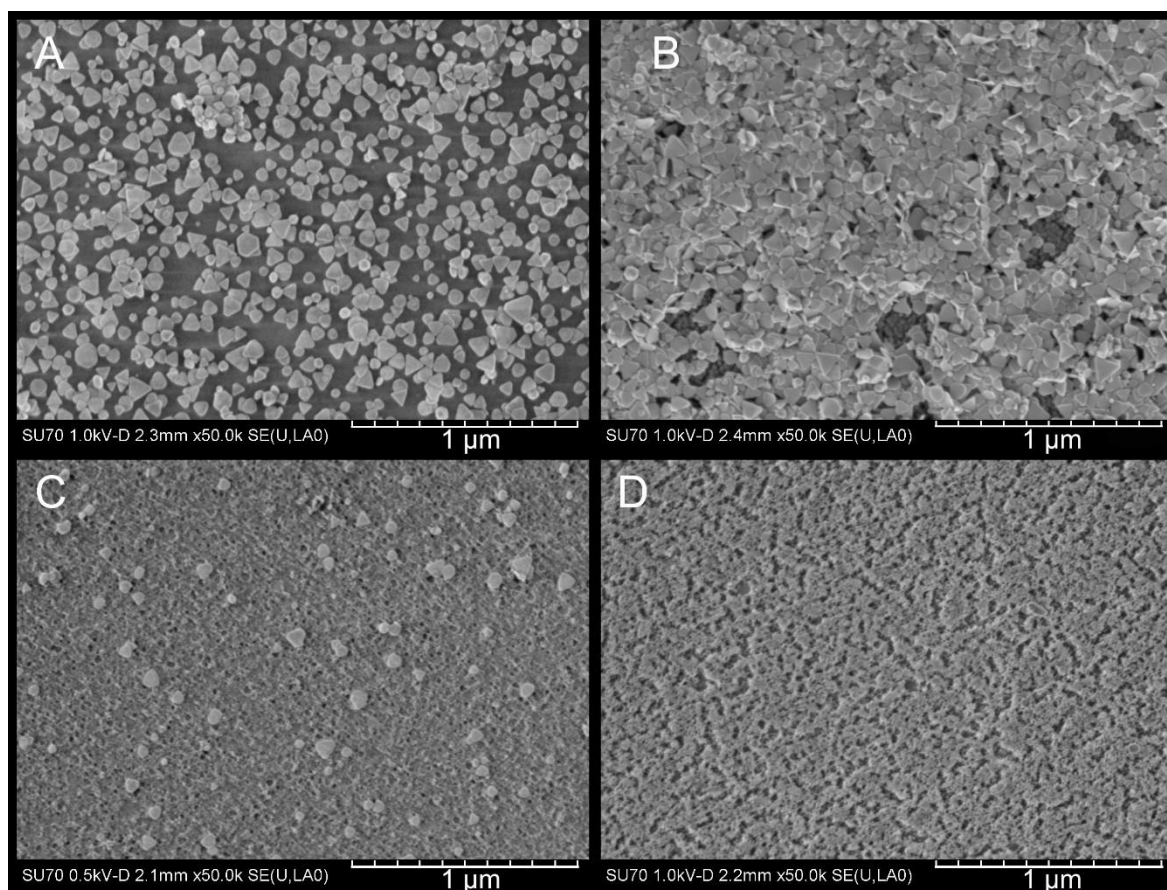


Figure 4. SEM images of Ag-silica composite coatings: silanized by APTES (A), AEAPTMS (B), MPTMS (C) and non-silanized (D)

Most even arrangement of Ag NPRs are visible on APTES functionalized coating – particles are arranged mostly as monolayer and noticeable aggregation is minimal. The image of AEAPTMS functionalized surface shows aggregation of particles and uniform layer no longer forms. Consequently, this layer of Ag NPRs looks grayish and no SPR is observable in UV-Vis spectra. Only separate, wide spread particles are observed on MPTMS functionalized coating. The UV-Vis spectra data show weak absorbance of unmodified coating and no Ag NPRs are observed on SEM image.

4. Conclusions

This research showed that most homogeneous silica-Ag NPRs coatings are obtained when surfaces were silanized with APTES. However, AEAPTMS silanized coatings tend to aggregation of silver NPRs, while MPTMS functionalized coatings have low affinity to Ag NPRs. Nevertheless, we successfully made functionalized silica coatings by sol-gel method and formed Ag NPRs layer on them via self-assembly process. This type of coatings can be applied for further research in SERS, or used for making multilayer coatings to obtain Ag NPR- silica embedded matrixes. On the other hand, the influence of

other surface parameters to Ag NPRs self-assembly, like surface roughness, silanization method and etc., should be further investigated.

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