



Article Electrochemical Fabrication of Inverse Opals of Silver with Cyanide-Free Electrolytes

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Abstract: Silver inverse opals were prepared electrochemically using non-toxic water–ethanol rhodanic and sulfite electrolytes for silver plating. Electrochemical crystallization of silver occurred in the pores of opal matrices made of 350 nm polystyrene microspheres. Samples with the most uniform structure and lowest percentage of surface admixtures were obtained from rhodanic electrolytes. Reflectance optical spectra of the silver inverse opals with a high surface periodicity showed various plasmon excitation modes in a visible spectral range making the silver opals attractive for plasmonics.

Keywords: silver; inverse opal; electroplating; electrolytes; X-ray photoelectron spectroscopy; surface plasmon resonance



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1. Introduction

Two-dimensional periodic nanostructures such as 2D photonic crystalline films are attractive for applications in various optical devices including mirrors [1], optical switchers [2], parts of optoelectronic devices [3], gas resistive sensors [4], optical sensors, and biosensors [5]. As well as optical sensors based on inverse opal films there are SPR [6] and SERS sensor platforms [7] which are attractive as for qualitative analysis and for structural investigations of biomolecules and cell compartments.

In the last decades, optical sensors based on plasmonic effects represented a new breakthrough in analytical chemistry as new chemical analytical techniques. Plasmonenhanced optical sensors, such as surface plasmon resonance spectrometry (SPR) and surface-enhanced Raman spectroscopy (SERS), have applied nanostructures of noble metals, including gold and silver, as "nanoantennas" [8,9]. Silver and gold nanoparticles increase the intensity of Raman spectra with high enhancement factors for up to 10¹⁴ as a result of the excitation of surface plasmon resonance in a visible range. Nowadays, the most popular materials for SPR and SERS detection are different kinds of nanocomposites with Ag and Au nanoparticles. At the same time, the highest enhancement factors are observed for so-called "hot spots" which are distributed stochastically. Moreover, the routine experiments with gold and silver nanoparticles have a low reproducibility [10].

Advantages of periodic nanostructures (so called "micro-array substrates") are uniformity and fabrication reproducibility [7]. Thus, SPR and SERS spectra collected using these substrates are stable and reproducible. The enhancement properties of the surfaces with periodic nanostructure can be tuned and optimized for particular applications. In addition, instead of the formation of "hot spots" the micro-array-based substrates cause the excitation of new plasmon modes in the visible spectrum [8,11–13]. On the other hand, the synthesis of periodic substrates is more complicated and expensive than the synthesis of colloids. Moreover, there are some difficulties in investigating and standardizing the surface of these substrates [12,13].

In the current manuscript we describe the results of a periodical nanostructure formation using an electrochemical approach. Plating of silver was carried out using polystyrene matrices as templates to form inverse opal structures. Solutions based on cyanide complexes of silver are widely used for electroplating. Deposits obtained with these solutions have perfect quality as mirrors, but the roughness of such films is low which is not optimal for plasmon-enhanced optical sensors. One of the most important disadvantages of cyanide electrolytes is their toxicity. Thus, plating solutions based on other silver complexes are under development nowadays.

In the present manuscript, inverse opals of silver were analyzed due to the lack of information about their optical characteristics in the literature. It is shown that plasmonic and optical properties of silver are suitable for application in different devices based on photonic crystals. Moreover, silver is a more cost-effective material than gold. For this reason, the application of silver can decrease the prices of the devices.

Two non-cyanide electrolytes (rhodanic, sulfitic) were used for the synthesis of silver inverse opals. Such electrolytes are stable at pH 3–7, can be used at room temperature, and have a high current efficiency and conductivity. These plating solutions are based on sufficiently stable silver complexes that have been reported elsewhere [14–17]. To improve the characteristics of electrolytes, water–alcohol solutions have been used to make polystyrene matrices moisten better. This approach has resulted in a controllable method which allows the synthesis of silver inverse opals of the required thickness.

According to the data presented in [18], the inverse opals of gold with a microsphere diameter of 350 nm and a normalized thickness of 0.4 ± 0.1 have the most suitable properties for application in plasmonic optical sensors. For this reason, we synthesized silver inverse opals with the same geometric parameters and also obtained the opals with a microsphere diameter of 440 nm. The normalized thickness was varied in order to study the influence of the sample morphology on optical properties.

2. Materials and Methods

Ag inverse opals were fabricated by the electrodeposition of silver into the void of opal matrices.

Layers of Ag and Au of 100 nm were deposited on the surface of indium tin oxide coated glass slide (ITO/glass) by magnetron sputtering using a Quorum Technologies Q150T Turbo-Pumped Sputter (Quorum Technologies, Laughton, UK). The opal matrices were made of polystyrene microspheres deposited on the surface of glass/ITO/Au substrates.

Three types of polystyrene microspheres with diameters of 340 ± 15 nm, 350 ± 30 nm, and 440 ± 20 nm were used for the formation of the matrices. The microsphere diameters were estimated according to scanning electron microscopy (SEM) data. The growth of the direct opals was carried out according to the procedure reported recently in [19–21].

Flat Ag films were electrochemically deposited onto the surface of glass/ITO or Ag/ITO/glass substrates. The process was carried out in a three-electrode cell and potentiostat-galvanostat Elins P-45X (Electrochemical Instruments, Chernogolovka, Russia) at room temperature using sulfitic and rhodanic electrolytes. The reference electrode was an aqueous Ag/AgCl/KCl(s) and a platinum plate of 2 cm² surface was applied as a counter electrode. The working and counter electrodes were placed parallel to each other and separated by a distance of 2 cm.

Electrochemical formation of inverse opals was carried out in the same three-electrode cell. Direct opal matrices were applied as working electrodes in this process [19,21]. After the electroplating process, the microspheres were removed chemically in toluene. The inverse opals with different thicknesses of 68–315 nm were prepared. Working potentials for the electrolytes (-0.1 V for sulfitic and -0.24 V for rhodanic) were determined using cyclic voltammetry. The charge required for the formation of the opal of a given thickness was calculated using Faraday's laws of electrolysis. Typical chronoamperometric curve for the process of the flat film and the opal formation are given in Figure 1.



Figure 1. Chronoamperometric curves for the process of silver deposition ((**a**) deposition on the flat glass/ITO/Au substrate (rhodanic electrolyte, U = -0.27 V), (**b**) deposition into the opal matrix on glass/ITO (rhodanic electrolyte)).

As principal reagents, potassium chloride (Rushim, "pur.", GOST 4234-77), ethanol 95% ("Medhimprom"), silver nitrate (Carl Roth, "puriss."; Lenreactiv, "puriss.", GOST 1277-75), ammonium rhodanide (Rushim, "pur."), sodium sulphide ("Rushim"), and distilled water were applied. Two kinds of electrolytes were prepared for silver electrochemical deposition:

H₂O: 6 g/L Ag, 72 g/L NH₄SCN, 2 M C₂H₅OH (rhodanic electrolyte).;

 $H_2O: 3-4 g/L Ag, 261 g/L Na_2SO_3, 2 M C_2H_5OH$ (sulphitic electrolyte).

The overall reaction for the deposition of silver is

$$[AgL_x] + e \to Ag + xL \tag{1}$$

where $L = SCN^{-}$, SO_3^{-} for rhodanic and sulfitic electrolytes, respectively.

Surface morphology of direct and inverse opals was examined using a Leo Supra 50 VP scanning electron microscope (Carl Zeiss, Oberkochen, Germany) and a Carl Zeiss NVision 40 scanning electron microscope (SEM) (Carl Zeiss, Oberkochen, Germany).

X-ray photoelectron spectroscopy and energy dispersive X-ray analysis were performed to detect impurities on the surface of the samples. X-ray photoelectron spectra were collected using Axis Ultra DLD spectrometer (Kratos Analytical, Manchester, UK). EDX analysis was carried out using a Leo Supra 50 VP scanning electron microscope with EDX Oxford Instrument attachments.

Optical properties of silver inverse opals were investigated by reflection and diffusion spectroscopy. The spectra were collected using a UV-vis spectrometer Lambda 950 (PerkinElmer, Norwalk, CT, USA) using a universal reflectance accessory (URA). Measurements were performed in a spectral range of 250–1000 nm with a scan step of 1 nm, 300–800 nm, and 300–800 nm with a scan step of 2 nm. Specular reflectance spectra with incidence angles of 8°, 30°, 45°, and 64° were collected for the inverse opal with the most uniform surface.

3. Results and Discussion

Micrographs of the silver films are shown in Figure 2. According to the SEM images, the average grain size of the films obtained using rhodanic electrolyte was larger than obtained from a sulfite electrolyte. The silver particles formed using a sulfite silver electrolyte had a round shape, and the particle size was 200–500 nm. Electrochemical silver plating from the rhodanic solution led to larger polyhedron crystallites (up to 1 μ m) with sharp edges. For the following formation of inverse opal films, the rhodanic silver electrolyte was taken because of the larger size of the crystallites that is more promising for full pore filling by crystalline silver and the formation of a more uniform inverse opal.



Figure 2. Micrographs of the Ag films obtained using (**a**) sulfite electrolyte on a glass/ITO/Au substrate, $E_d \sim -0.1$ V to Ag | AgCl | KCl(sat.), and (**b**) rhodanic electrolyte on the surface of glass/ITO/Au substrate, potential of deposition~-0.27 V to Ag | AgCl | KCl(sat.).

According to the EDX data (Table 1), the silver flat films did not contain any impurities. Elements Al, Si, Ca, and In are components of the substrate (glass and ITO) which was coated with the layers of Au and Ag films for better adhesion.

Table 1. EDX data of the Ag film obtained using rhodanic and sulfitic electrolytes.
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Substrate	Electrolyte	Element	At. %
glass/ITO/Au	Rhodanic	Ag	59.2 ± 11.8
Ū.		Si	11.2 ± 2.2
		Ca	2.1 ± 0.4
		Al	2.0 ± 0.4
		In	8.5 ± 1.7
		Au	17.0 ± 3.4
glass/ITO/Au	Sulfitic	Ag	35.8 ± 2.9
		Si	21.4 ± 1.3
		Ca	4.0 ± 0.1
		In	13.3 ± 0.6
		Au	25.5 ± 1.0

XPS data of the silver flat films are given in Table 2. As a surface characterization method, the XPS spectra demonstrate the presence of metal silver Ag^0 , and silver ions Ag (I), most likely, stable silver sulfide and silver sulfate. Products such as Ag_2S and Ag_2SO_4 could be formed as a result of silver oxidation in air [22]. Compared to the products for the silver iodide electrolyte, no additional valent states of silver were found.

Normalized thickness *w* of the inverse opals (Figure 3) was calculated using the SEM micrographs of the samples (Figure 4). The data of statistical analysis showed that the average diameters of the voids *d* on the opal surface were 249 ± 17 nm, 263 ± 16 nm, 247 ± 19 nm, 256 ± 35 nm, and 385 ± 55 nm for the five different samples, respectively. The ordered areas in the samples were up to 5 µm.



Figure 3. Scheme of the Ag inverse opal ((a) conductive plate (e.g., Ag/ITO/glass), (b) silver layer with the thickness *t*, (c) spherical void with diameter *D*, *d*—diameter of the holes that was measured on the SEM images).

Substrate	Electrolyte	Binding Energy, eV (Ag 3d _{5/2})	Valence State of Ag	At. % (of All States of Ag)
glass/ITO	Rhodanic	368.0, 368.4	Ag	68.3
entry 2	data	368.6	Ag (I) (Ag ₂ S)	31.7
glass/ITO/Ag		368.1, 368.5	Ag	43.3
	Rhodanic	368.8	Ag (I) (Ag ₂ S)	56.7
ITO/glass		368.1	Ag	50.0
	Sulfite	368.7	Ag (I) (Ag ₂ S)	33.3
		367.8	Ag (I) (Ag ₂ SO ₄)	16.7
Ag/ITO/glass		368.2, 368.3	Ag	40.0
	Sulfite	368.8	Ag (I) (Ag ₂ S)	43.3
		367.9	Ag (I) (Ag_2SO_4)	16.7

Table 2. XPS data valence states of the Ag for the films deposited using rhodanic and sulfite electrolytes.

The electroplating quality factor was found as $\Delta w/w_{\text{theor}}$ ratio to characterize the uniformity of the film thickness in the plane. Generally, the opal films deposited with a sulfite silver electrolyte were of lower quality factor in comparison with the samples obtained with the rhodanic silver electrolyte. In the case of the sulfite silver electrolyte, the dendric growth of silver was more dramatic. The Ag-4 sample was of the highest quality according to the quality factor and SEM images. More detailed information about the samples is given in Table 3.

Table 3. Characteristics of silver inverse opals (exp.—experimental values measured on the SEM images or calculated according to the experimental data, theor.—theoretical values-calculated according to Faraday's laws of electrolysis under the assumption that the direct opal matrix had no defects).

Name	Ag-1	Ag-2	Ag-3	Ag-4	Ag-5
Electrolyte	Rhodanic	Rhodanic	Rhodanic	Rhodanic	Sulfitic
$d_{\rm exp}$, nm	247 ± 19	256 ± 35	385 ± 55	263 ± 16	249 ± 17
<i>D</i> , nm	340 ± 15	340 ± 15	440 ± 20	350 ± 30	350 ± 30
Charge, mC -	-16	-211	-181	-11	-133
Theoretical $w = t_{\text{theor}}/D$	0.2	0.5	1	0.7	0.7
Experimental $w = t_{exp}/D$	0.2	0.2	0.7	0.8	0.9
$\Delta w / w_{\text{theor}} * (\Delta w = w_{\text{theor}} - w_{\text{exp}})$	0	0.6	0.3	0.14	0.29

* average $\Delta w / w_{\text{theor}} = 0.27$.

The conclusions about the periodicity of the samples surface were made using Fast Fourier transform of the opals SEM images. It was empirically established that the samples with large, ordered areas had Fourier images with six distinct minima, the opals with "middle" ordered areas had at least three rings on the Fourier images, and the samples with a disordered surface did not have any distinct minima or rings on the Fourier images. Five samples with their Fourier images are arranged in ascending order of the surface periodicity in Figure 4.

Specular reflectance spectra for the inverse opals are given in Figure 5. The complexity in the spectra originated from three factors that influenced the specular reflectance of inverse opal films. These factors are periodicity of the surface, thickness of opal layer, and presence of dendrite silver growth. Increase in thickness led to a decrease in specular reflectance so we observed the low intensity spectrum for the finest film Ag-1 (w~0.2). Dendrite growth and disordered areas increased the proportion of diffuse reflection that led



to a decrease in specular reflectance. This factor resulted in a low intensity of the spectrum for Ag-2.

Figure 4. Micrographs of the Ag inverse opals with their Fourier images: (**a**,**b**) Ag-1, (**c**,**d**) Ag-2, (**e**,**f**) Ag-3, (**g**,**h**) Ag-4, (**i**,**j**) Ag-5.



Figure 5. Specular reflectance spectra of the Ag inverse opals (the spectra were collected for five samples under equal incidence angle $\sim 8^{\circ}$).

The presence of larger or smaller ordered areas (domains) on the sample surface was mainly caused by the periodicity of the initial polystyrene matrix. The sample Ag-4 with the largest ordered areas on the surface, the highest thickness value (w~0.8), and the smallest amount of dendric growth had the highest specular reflectance and the most pronounced reflectance minimum at $\lambda = 340-420$ nm among the five samples.

The amount of dendric growth determines the smoothness of the sample surface. Thus, the highest specular reflectance for the sample Ag-4 was mainly caused by the presence of large, ordered areas and by the smallest amount of dendric growth.

The presence of large, ordered areas resulted in the excitation of special plasmon modes in the samples. It led to the enhancement of the electromagnetic field near the sample surface and also increased the specular reflectance. The presence of reflectance minima could also be associated with these plasmon modes.

A similar profile with a wide minimum was in the spectrum of Ag-3 (w~0.7). The red shift of the plasmon resonance minimum to 620–750 nm originated from the largest diameter of microspheres (440 \pm 20 nm) and the 2D period, respectively. The larger width value could be explained by a decrease in characteristic size of ordered areas according to the corresponding SEM and Fourier images (Figure 4e,f). In each spectrum, the minimum at the wavelength 300–320 nm corresponded to the reflectance minimum of ITO.

Specular reflectance spectra for the sample Ag-4 were collected under different incidence angles ψ (Figure 6). The minima that do not move with the change of the incident angle correspond to localized (Mie) surface plasmons according to Kelf et al. [23]. The minima that change their position occur due to the mixing of surface plasmons. According to the data for the Ag-4 sample, localized surface plasmons were excited at the wavelengths 340–520 nm and 440–520 nm (minima in violet rectangles, Figure 6). At the same time, the presence of mixed plasmons in spectra of silver opals is under discussion because the shift of minima with incidence angle ψ was not obvious as in case of gold inverse opals [19]. On the other hand, the results were in good agreement with data reported for silver inverse opals by Bartlett et al. [24].



Figure 6. Specular reflectance spectra of the sample Ag-4 collected under different incidence angles.

4. Conclusions

Silver inverse opals were synthesized using non-cyanide rhodanic and sulfitic waterethanol plating solutions. It is shown that the method described in the present work allows silver opals of 0.5–0.9 *w* thickness to grow on glass/ITO/Au substrates. In addition, the degree of order of the 2D opals determines plasmonic characteristics of the films. For the samples with large, ordered areas, the more pronounced minima on reflectance spectra at 370–460 nm were observed, and the enhancement of electromagnetic field was higher than for the samples with smaller domains. Such films could be promising for plasmonicenhanced optical sensors with excitation lasers of 340–420 nm and 440–520 nm wavelengths as a result of resonance effects.

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