Supporting information

Photo-Induced Self-Assembly of Silver Nanoparticles for Rapid Generation of First and Second Surface Mirrors

Etienne Caillosse^{1,2}, Mohamed Zaier², Mariam Mezghani², Samar Hajjar-Garreau², Loïc Vidal², Daniel Lougnot³, Lavinia Balan^{1,2}*

¹Université d'Orléans, Conditions Extrêmes Matériaux Haute Température et Irradiation CNRS UPR 3079, F-45000, Orléans, France

²Université de Haute Alsace, Institut de Science des Matériaux de Mulhouse CNRS UMR 7361, F-68100, Mulhouse, France

³Université de Haute Alsace, Centre de recherches sur les Economies, les Sociétés, les Arts et les Techniques CRESAT EA 3436, F-68100 Mulhouse, France

*Corresponding author: E-mail: lavinia.balan@cnrs-orleans.fr; Tel: +33(0)23825565

Characterizations by atomic force microscopy (AFM) were performed on three different samples with three thicknesses of silver: 350, 150 and 50 nm. The thicknesses were determined by the difference in altitude corresponding to a scratch made on the silver film with a hard tip. Figure S1 below shows 2D projections, images of the air side of the samples



300.0

200.0

at the scratch and the corresponding 2D projections of the samples at 350 nm, 150 nm and 50 nm.



20

30

<u>و</u> 150 م 100

50

0

0

10

x (µm)

20

Figure S1. AFM images of the air side of the samples at the scratch and its corresponding 2D projections of a) 350 nm thick, b) 150 nm thick and c) 50 nm thick.

The chemical composition of the synthesized AgNPs film was determined by energy dispersive spectroscopy (EDS) (see Figure S2). A high percentage of silver with traces of gold, which result from the gold metallization phase prior to SEM analysis. There are also

some weak peaks of O, C and Si originating from the photolysis of the generator of free radicals and from the glass substrate, respectively.



Figure S2. EDXS spectrum of the nanomaterial.

Samples were also analyzed by X-ray photoelectron spectroscopy (XPS). XPS is a surfacesensitive analytical technique useful not only for the identification of elements present in the sample but also for determining their oxidation states. Figure S3 shows the wide scan survey spectrum and a very intense double peak whose binding energy position corresponds to the spin–orbit splitting components Ag $3d_{5/2}$ and Ag $3d_{3/2}$ (Ag $3d_{5/2}$ at 368.30 eV and Ag $3d_{3/2}$ at 374.30 eV).



Figure S3. XPS spectrum of the surface of the silver nanoparticles coating film a) XPS survey spectrum, b) XPS spectrum for Ag (0) $3d_{5/2}$ and $3d_{3/2}$.

Figure S4 shows XPS peaks of C and O, which correspond to photoproducts resulting from the photolysis of the generator of free radicals in the liquid formulation. A weak signal indicative of traces of N in the metallic film was also detected.



Figure S4. XPS spectrum for C1s, N1s and O1s.

Table S1 summarizes the results recorded with a series of mirror samples obtained from a variety of formulations, which clearly confirms that Ag(0) is always the most predominant element at the surface of the sample, regardless of the solvent used to prepare the photosensitive formulation. The important signal associated to carbon observed in Table S1 deserves a few comments. XPS is known to provide extremely weighted information from the outermost layer. Moreover, it is almost impossible to prevent the measured data from being seriously affected by surface contamination [1]. As a consequence, mostly the outermost layer is inhomogeneous and the composition is different from the bulk. It is therefore almost impossible to figure out the total composition of the outermost layer correctly. Based on the composition of the formulations used, the atomic abundance of silver is about 9 times that of carbon. A first point that must be taken into account in the analysis of the XPS response of these two elements is the large difference between the inelastic mean free paths (lambda) of the electrons whose kinetic energies correspond to Ag $3d_{5/2}$ (1120 eV) and C 1s (1200 eV). They are 16 Å [2] and 35 Å [3, 4], respectively. From this, it can be inferred that the probed

thickness for the element carbon is about twice that of silver, which partly explains the abnormally high signal of carbon in all the samples studied.

Table S1. XPS results for samples synthesized with different solvents and the relative atomic

 percentage of chemical elements.

Name /	Solvent	Position	H ₂ O	EtOH	H ₂ O/C ₂ H ₅ OH (% At)	CH ₃ CN	H ₂ O/CH ₃ CN
Ag 3d	Ag 3d _{5/2}	368.30	44.88	41.63	55.15	32.96	37.66
C1s	CC CH	284.34	33.72	29.96	26.40	41.92	36.74
C1s	С=О	287.73	4.60	4.61	4.01	4.78	4.31
C1s	C-0	285.41	3.40	4.02	2.93	5.49	5.51
O1s	СО	530.92	9.08	8.53	8.44	10.48	9.83
O1s	NO ₃ ⁻	532.31	3.24	8.44	2.30	3.27	4.46
N1s	NO ₃ ⁻	406.02	1.08	2.81	0.77	1.10	1.49

However, this difference alone is not sufficient to fully account for the experimental observations. The other idea that comes to mind would be an inhomogeneous distribution of the carbon element throughout the thickness of silver films; in fact, carbon would be "excluded" from the depths of the film and would concentrate near the outermost surface. Thus, the thin superficial layer of the sample probed by XPS would be abnormally rich in carbon, which justifies the high values reported in Table S1.

Table S2. Spurious Fresnel reflectivity for borosilicate glass under an incidence of 8° (Calculations were carried out using Cauchy coefficients A = 1.5046 and B = 0.0042).

Wavelength (nm)	300	400	500	600	700	800	900	1000
Refractive index	1.551	1.531	1.521	1.516	1.513	1.512	1.510	1.509
Fresnel reflectivity (%)	4.8	4.5	4.4	4.3	4.3	4.3	4.2	4.2

The reflectivity of the glass/silver diopter was evaluated directly on the as-prepared samples, without any further processing. The reflectivity was measured through the supporting glass plate between 300 and 1000 nm as shown in Figure 5 on thick samples (ca 350 nm) for five different solvents (Table S3).

Table S3. Percent reflectivity	y of the samples	(a) 450 nm	for five	different solve	ents
	,				

Colventa	Reflectivity (%)		
Solvents	at A = 450 nm		
100 % H ₂ O	88 %		
100 % C ₂ H ₃ OH	64 %		
100 % CH ₃ CN	54 %		
$80 \% H_2O + 20 \% C_2H_5OH$	83 %		
80 % H ₂ O + 20 % CH ₃ CN	94 %		

The adhesion of the silver layer on glass substrates was evaluated with a "Tape test" (Figure S5). This common test is widely used in the industrial world to evaluate the adhesion of coatings deposited on a variety of surfaces (described by ASTM D3359 and ISO 2409).

a)	b)	c)
-		

Figure S5. Images of the air-side sample 350 nm thick a) before etching the grid, b) before applying the adhesive tape and c) after peeling off the adhesive tape.

The contact angles of water on silver films were measured. Figure S6 below shows two samples: a) 150 nm and b) 50 nm thick. The insertion images correspond to a drop of water on the substrate inclined at 20°. The contact angles measured on the air side are $91^{\circ} \pm 3$ and $87^{\circ} \pm 4$ for 150 and 50 nm films, respectively. As predicted by the Wenzel model, the drops are stable and do not slip when the holder is tilted by 20°.



Figure S6. Images of the water drops on silver films a) 150 nm thick film (insert, 20° inclined support) and b) 50 nm thick film (insert, 20° inclined support).

Additional photos of the as synthesized mirrors.



References:

[1] Hidetaka, K. X-ray Photoelectron Spectroscopy. *Materials Science and Engineering of Carbon*, 2016, 8, 153-171. DOI: 10.1016/B978-0-12-805256-3.00008-8

[2] Shinotsuka, H.; Tanuma, S.; . Powell, C. J.; Penn, D. R. Calculations of electron inelastic mean free paths. X. Data for 41 elemental solids over the 50 eV to 200 keV range with the relativistic full Penn algorithm. *Surf. Interface Anal.*, 2015, 47, 871–888. DOI: 10.1002/sia.5789

[3] Tanuma, S.; Powell, C. J.; Penn, D. R. Calculations of electron inelastic mean free paths (IMFPS). IV. Evaluation of calculated IMFPs and of the predictive IMFP formula TPP-2 for

electron energies between 50 and 2000 eV. Surf. Interface Anal., 1994, 21, 165–176. DOI: 10.1002/sia.740210302

[4] Zemek, J.; Houdkova, J.; Jiricek, P.; Jablonski, A.; Jurka, V.; Kub, J. Determination of electron inelastic mean free paths for poly[methyl(phenyl)silylene] films. *Polymer*, 2009, 50, 2445–2450. DOI: 10.1016/j.polymer.2009.03.031