

In Situ Growth of Vertically Aligned Gold Nanoparticles within Functionalized Polyvinylidene Fluoride Nanochannels for Optical Property Tuning

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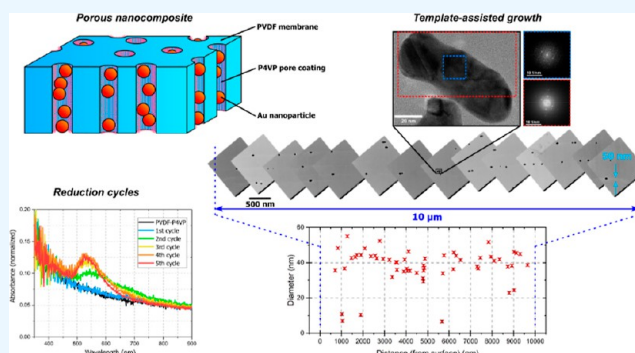
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ABSTRACT: A solid synthetic pathway for the localized formation of vertically aligned and well-distributed individual gold nanoparticles (AuNPs) in transparent ion-track-etched polyvinylidene fluoride membranes is herein reported. After a successful preconcentration of the Au(III) precursor within the functionalized cylindrical nanochannels of these membranes, *i.e.*, ion-track-etched radiografted with poly(4-vinylpyridine) (P4VP), a Au(III)-to-Au(0) chemical reduction was performed to in situ grow AuNPs inside the nanopores. Four classical reducing agents [ascorbic acid, hydroquinone, sodium citrate, and sodium borohydride (NaBH_4)] were studied, which led, at first glance, to similar composites. The reducing power of each reducing agent has been shown to affect the AuNP nucleation and growth processes. At room temperature, the reduction led to the synthesis of well-dispersed AuNPs along the whole pore length, with the exception of sodium citrate, which was found to be too weak to reduce efficiently the gold precursor. When energy was provided to the system by operating the reaction at 70 °C, the reduction was boosted and the synthesis with sodium citrate gave similar results to those obtained with the other reducing agents at 20 °C, *i.e.*, well-distributed AuNPs of around 30 nm of mean size. Increasing the number of reduction cycles resulted in an increase in AuNP size and, in the case of hydroquinone, in the elongation of the gold nanocrystals. This phenomenon was attributed to template-assisted AuNP growth in the nanopores. Despite the low amount of gold in the material (less than 0.2 %), the alignment of individual AuNPs all along the high aspect ratio nanopores (50:10,000) had a significant effect on the optical properties of the whole material, with the appearance of plasmonic properties for the nanocomposite membranes (λ_{plasmon} around 530 nm) and a further decrease of the effective refractive index of the nanoporous membranes.



1. INTRODUCTION

Nanocomposite materials, made from both organic and inorganic phases, allow the design of multifunctional materials, which are of great interest for the future technological development. Particularly, plasmonic-based nanocomposites, made from the dispersion of plasmonic nanostructures within a polymer organic matrix, have been studied for their optical properties that can lead to applications in (bio)sensing,^{1–3} catalysis,^{4,5} or even the development of a new category of so-called “metamaterials”^{1,6} for optoelectronics. In such materials, the polymer matrix confers its thermomechanical properties while the plasmonic components act as nanoresonators to affect the optical properties of the whole material.

In nanocomposites, the nanostructure is often the key to control and tune the material properties, especially since it drives the dispersion of the nanocomponents within the matrix, as well as their organization, which can trigger synergetic effects and, thus, enhance the optical response.⁶ To this end, organic polymers are convenient flexible matrices, due to the diversity of chemical functions and physical properties they can provide,

such as transparency⁷ or thermal properties,⁸ and their versatility in fabrication and structural processing, sometimes occurring spontaneously as in the case of self-assembly.^{9,10}

Among many advantages, such as high chemical resistance, high thermal stability, ferroelectricity, and easy processability due to its thermoplasticity, polyvinylidene fluoride (PVDF) is also well-known for its transparency in the whole UV–visible wavelength range. Recently, to reduce energy consumption in material processing, new preparations of highly transparent PVDF-based polymer films, dealing with a polymer mixture, cold-drawing technique,¹¹ or even nanoparticle (NP) inclusion,¹² have been extensively investigated to extend its applicability. A very recent work¹³ has shown that transparency

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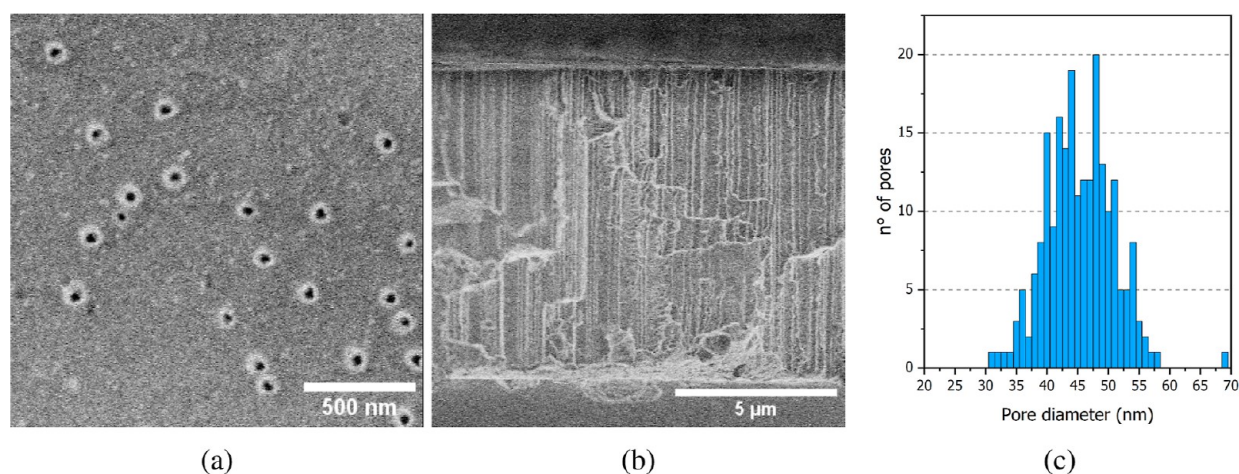


Figure 1. SEM images of (a) the surface and (b) the cross-section of a P4VP-g-PVDF membrane formed by track-etching of a PVDF film irradiated with an ion fluence of 10^9 cm^{-2} ; (c) the corresponding size distribution for the pore diameter (over 200 pores).

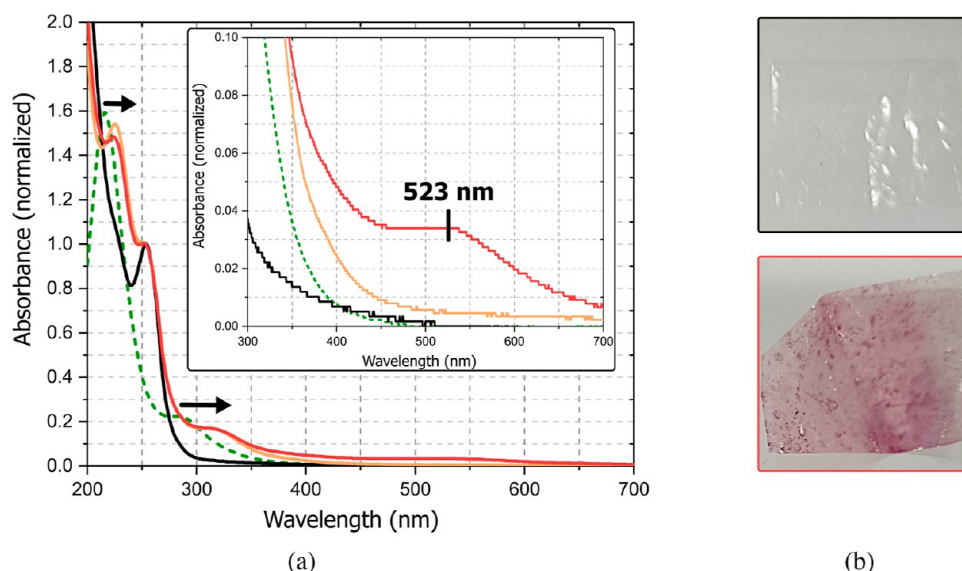


Figure 2. (a) Example of obtained UV–visible absorption spectra for a P4VP-g-PVDF membrane (black) before, (orange) after immersion in the gold salt for 24 h, and (red) subsequent reduction in NaBH_4 for 30 min. The gold salt (HAuCl_4) spectrum (green) is shown for comparison. The inset shows the zoomed-in image of the plasmon resonance band appearing after the reduction; (b) pictures of the same membrane showing the change in color between (top) before and (bottom) after AuNP synthesis.

is even higher when the PVDF films are irradiated with γ -rays, due to cross-link formation.

Irradiation with ionizing beams, notably swift-heavy ions (SHI), has proven to be an efficient way to both nanostructure solid PVDF films¹⁴ and functionalize them.^{15–17} During SHI irradiation, each ion impact creates very local zones of defects, so-called latent tracks, in the solid target materials. After a chemical attack, the latent tracks are partially removed, revealing cylindrical nanopores of very high aspect ratio. Typically, pore diameters of 50 nm over a tenth of micrometer in length, corresponding to the initial film thickness crossed over by the SHI, can be easily obtained. These ion-track-etched polymer membranes may be used as host sites for the inclusion of inorganic nanostructures through various processes¹⁸ such as direct inclusion of preformed NPs² or *in situ* template synthesis by electrodeposition^{19,20} or electroless deposition, *i.e.*, chemical reduction.^{21–26} In the case of template synthesis, *i.e.*, *in situ* growth of the inorganic nano-objects within the pores, a nucleation area is required in order to attract and catalyze the

growth of the nanocrystal within the structure. This nucleation area can be a metallic electrode in the case of electrodeposition or metallic catalyzing ions, usually Ag or Pd, distributed all along the pores and serving as nucleation sites for the electroless processes. To form these nucleation sites, a sensitization process is performed by first coordinating Sn(II) ions onto the pore surface, which will allow the entrapment of these catalyst ions.²⁷

The key parameter to enhance even further the optical properties of such nanocomposites is the multiscale spatial arrangement of the nano-objects within the matrix.^{28–30} To this end, various processes have been developed over the last decades to trigger and notably control *via* self-assembly the alignment of gold plasmonic NPs.^{31–34} The general idea is to further implement the anisotropy in the material, as it is usually required for tuning the final physical properties.^{33,35} To go beyond, in such architecture, it would be beneficial that the shape of the nano-object itself displays an elongated morphology. Gold nanorods have effectively been investigated due to the impact of their aspect ratio on their optical properties,

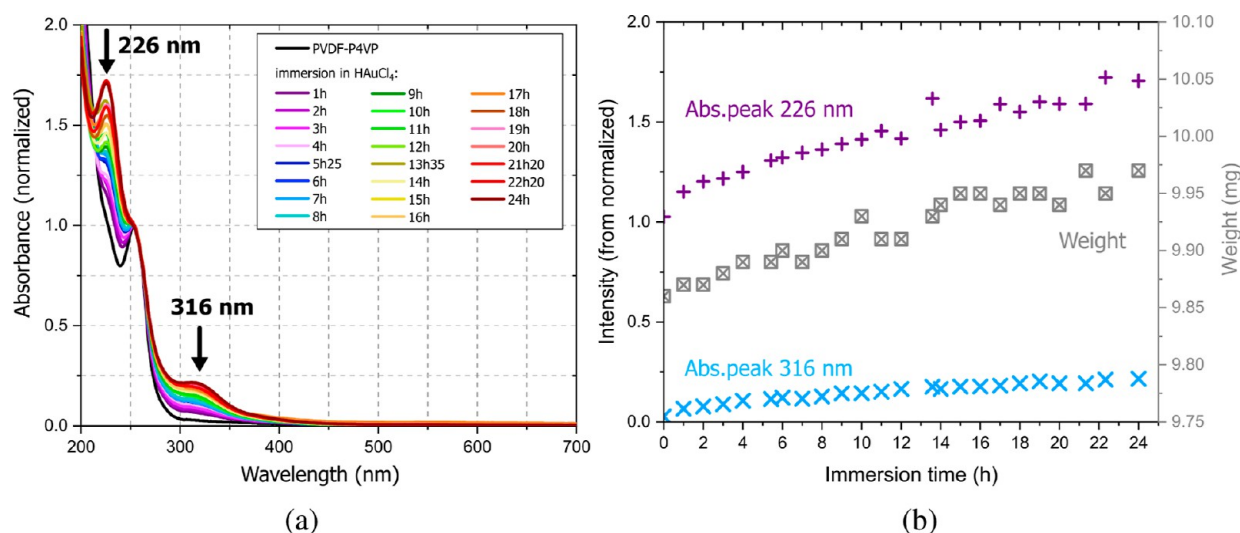


Figure 3. Kinetics of Au(III)-loading in P4VP-g-PVDF membranes: (a) UV–visible spectra of the P4VP-grafted PVDF membrane before (black) and after loading with HAuCl₄ over 24 h (purple to brown) ; (b) weight (grey squared times) and HAuCl₄ absorption peaks at 226 nm (violet +) and 316 nm (blue x) evolution with immersion time.

Table 1. Weight Gain (Δw) from the Initial P4VP-Grafted Membrane with Au(III) and Cu(II) Loading over Immersion Time and Determination of the Membrane Pore Filling

metallic salt	immersion time (h)	1	4	8	12	16	20	24
HAuCl ₄	Δw (μg) ^a	10	30	40	50	90	80	110
	% pore filling	2.55	4.65	10.20	12.75	22.96	20.06	28.06
CuSO ₄	Δw (μg) ^a	10	40	50	50	30	60	40
	% pore filling	2.46	9.84	12.30	12.30	7.38	14.76	9.84

^aDifference from the initial PVDF–P4VP membrane before immersion.

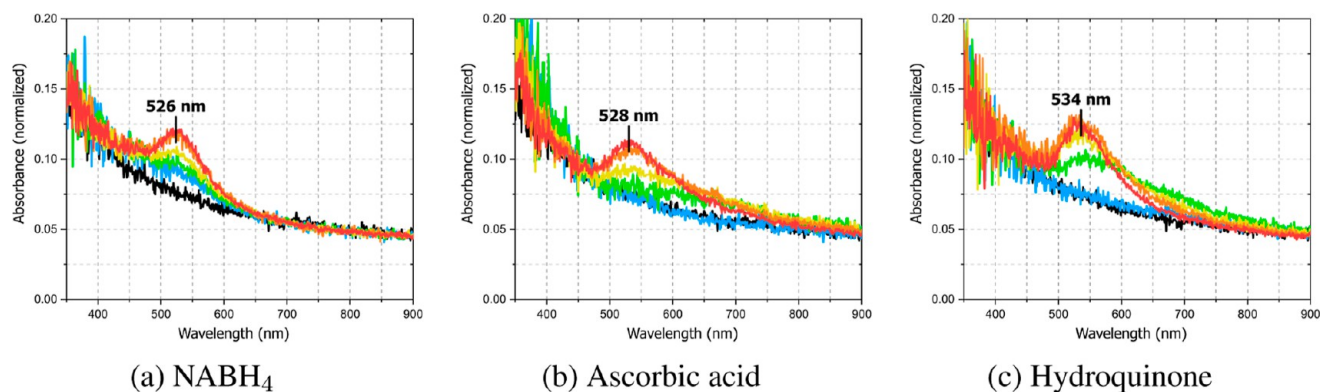


Figure 4. UV–visible spectra of the Au(III)-loaded P4VP-g-PVDF membrane (black) before and after [(blue) 1st, (green) 2nd, (yellow) 3rd, (orange) 4th, and (red) 5th] successive reduction cycles using (a) NaBH₄, (b) ascorbic acid, or (c) hydroquinone as a reducing agent.

such as bimodal plasmonic response.^{36,37} These nano-objects are usually synthesized in solution prior to incorporation in the matrix, which may hinder further organization.

To address the challenge of aligning elongated individual gold NPs in an oriented direction, the originality of this work lies in the use of a host nanoporous PVDF transparent matrix as a template to guide the growth and shape of the individual gold NPs.

To this aim, we describe the direct chemical synthesis of plasmonic gold NPs aligned within the poly(4-vinylpyridine) (P4VP)-radiografted nanopores of ion-track-etched PVDF membranes. Contrary to most electroless growth of inorganic nanostructures within membranes,²⁶ the present synthesis was free from previous steps of sensitization and allowed the direct

formation of gold NPs (AuNPs) along the membrane pores. The role of the reducing agent used, as well as the heating, in the NP size and distribution through the membrane thickness was investigated, and elongated-shaped NPs, formed by the template effect, were even reported in a specific case. Cycling steps, *i.e.*, a repetition of the loading in Au(III) ions and subsequent reducing phases, were also addressed to show how these steps might affect the size and the shape of the gold nanocrystals. AuNPs pore filling percentages were estimated from scanning electron microscopy (SEM) and gravimetry. A deeper structural characterization was done by transmission electron microscopy (TEM) and a fast Fourier transform (FFT) diffraction pattern. A 2D mapping made of multiple TEM images reconstruction of

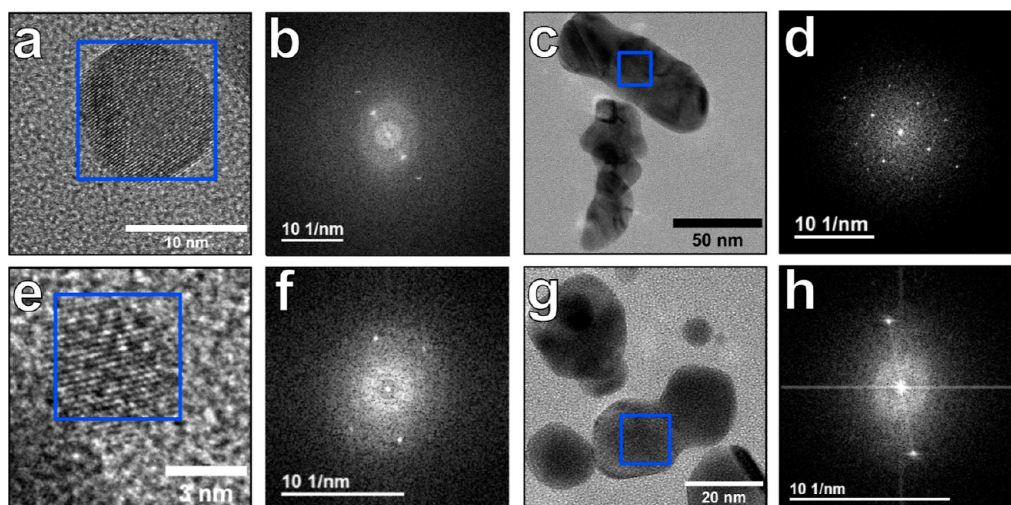


Figure 5. (Top) TEM pictures of AuNPs within a P4VP-g-PVDF membrane after (a) 1 and (c) 5 reduction cycles using hydroquinone and (b,d) the respective FFT performed on the blue square areas; (bottom) TEM pictures of AuNPs within a P4VP-g-PVDF membrane after (e) 1 and (g) 5 reduction cycles using NaBH_4 and (f,h) the respective FFT performed on the blue square areas.

Table 2. Interplanar Distance for Plane (111), $d_{(111)}$, and Lattice Parameter, a , Determined for AuNPs Synthesized within P4VP-g-PVDF Membranes after 1 and 5 Cycles, Using Hydroquinone or NaBH_4 as a Reducing Agent

reducing agent	no. of reduction cycles	$d_{(111)}$ (nm)	a (nm)
hydroquinone	1 cycle	0.233	0.404
	5 cycles	0.239	0.413
NaBH_4	1 cycle	0.232	0.403
	5 cycles	0.238	0.411

Table 3. Standard Redox Potentials (vs Standard Hydrogen Electrode) for the Reducing Agents of This Study

reducing agent	E^0 (V vs SHE)
sodium citrate	−0.180 ⁴⁴
ascorbic acid	−0.390 ⁴⁵
hydroquinone	−0.699 ⁴⁴
NaBH_4	−1.240 ⁴⁶

the entire composite film thickness of 10 μm allowed us to spatially estimate the AuNPs distribution.

To characterize the optical properties of the resulting nanocomposite membranes, absorption, transmission, and reflectance spectra were recorded, thanks to an integrating sphere, allowing us to distinguish the diffuse reflectivity from the specular one. Finally, taking into account the individuality of well-distributed and monodisperse aligned AuNPs within the PVDF matrix, an adaptation of the Lorentz–Lorenz equation for ternary systems is herein proposed to extrapolate the effective refractive index in such nanocomposites.

2. RESULTS AND DISCUSSION

2.1. *In Situ* Synthesis of AuNPs within a Transparent P4VP-g-PVDF Nanoporous Membrane

The incorporation of AuNPs within the P4VP-g-PVDF membrane was performed by the *in situ* chemical reduction of a gold precursor (chloroauric acid: HAuCl_4), previously loaded in the membrane (Scheme 1).

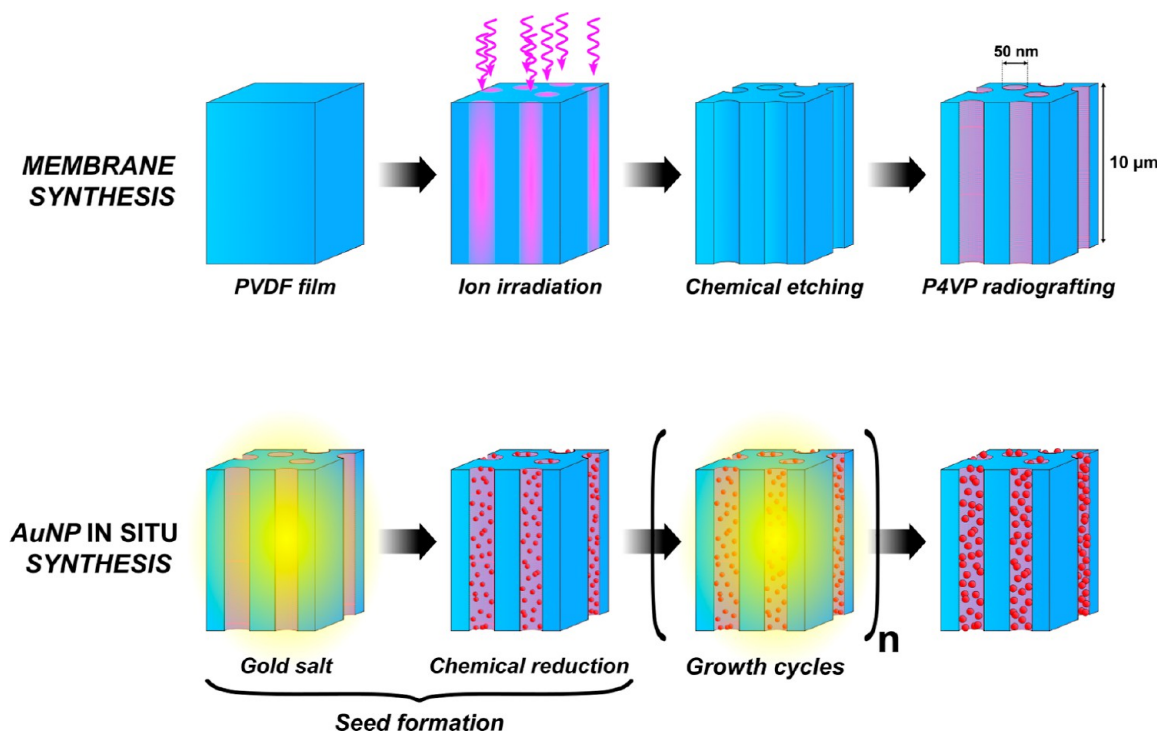
P4VP-g-PVDF track-etched membranes were prepared following an already reported synthesis based on the ion-track-

etching technique³⁸ (see Experimental section). The pore density was 10^9 cm^{-2} , and the mean pore diameter was $45 \pm 6\text{ nm}$ (Figure 1). As described previously³⁹ in similar experimental conditions, it was shown, thanks to streaming potential measurements, that P4VP grafting has homogeneously covered the whole nanopore walls.

These functionalized P4VP-g-PVDF nanoporous membranes were first immersed in a 0.01 M aqueous solution of HAuCl_4 and then rinsed with deionized water and dried (Gold salt step in Scheme, bottom). As-cleaned Au(III)-loaded membranes were in turn immersed in a reducing agent to trigger the reduction into Au(0) NPs. The reduction is effective, as shown by the change in the membrane color from transparent to red/purple, in agreement with the appearance of the absorption band at 523 nm corresponding to the plasmon resonance (λ_{plasmon}) of spherical AuNPs (Figure 2).

2.1.1. Percentage Evaluation of Pore Filling with Gold Metallic Salt. Prior to reduction, the loading process with gold chloride (HAuCl_4) was investigated over 24 h of immersion. UV–visible absorption spectroscopy (Figure 3a) showed that two absorption bands appeared in the near-UV region at 226 and 316 nm. These bands are in accordance with the two characteristic absorption bands of HAuCl_4 at 216 and 286 nm.⁴⁰ The slight red shift for these bands (black arrows in Figure 2a) can be explained by the coordination of Au(III) ions with the pyridine group of the P4VP, which eases the electronic delocalization, thus lowering the energy of the absorption bands, or by a local disturbance of the refractive index due to the overall PVDF environment. UV–visible absorption spectroscopy also evidenced that the absorption peak intensities attributed to HAuCl_4 at 226 and 316 nm were increasing quasi-linearly over the time of immersion. This increase had been related to the sample weight gain, which was therefore attributed to the sole presence of Au salt. From electron microscopy measurements (pore diameter, length, and density), it was possible to correlate the pore volume fraction to the Au(III) content and to estimate the Au(III) filling percentage in the membrane porosity. Similar loading of the pores of P4VP-g-PVDF membranes with copper sulfate, under the same conditions, was also carried out. Table 1 summarizes the obtained percentage of filled porosity with gold and copper ions as a function of the immersion time in salt

Scheme 1. (Top) Scheme of the Various Steps for the Formation of the Nanoporous P4VP-Grafted PVDF Membrane and (Bottom) of the AuNP In Situ Chemical Synthesis within Its Pores



solution. After 24 h, almost a third of the porosity (28%) is filled with the gold salt, while copper salt led to membrane filling over time that peaked only at 15% after 20 h of immersion. This difference in loading is due to a better affinity of Au(III)⁹ than Cu(II) with the P4VP pyridine groups present on the surface of the pores.

2.1.2. Effect of Loading/Reduction Cycling. The reduction process can be assimilated to a nucleation cycle, *i.e.*, a first synthesis of nanocrystals acting as seeds. It is afterward possible to repeat this cycle by immersing again the seed-containing membrane into the gold salt and then into the reducing agent. These additional cycles are growth cycles since they favor the AuNP growth within the nanopores. Up to 5 cycling steps were carried out in these syntheses in order to investigate further the effect on the crystal growth (Figure 4). The increase in intensity for the plasmon resonance absorption bands at 526, 528, and 534 nm, in the case of NaBH₄, ascorbic acid, and hydroquinone, respectively, can be related to an increase in size and content of AuNPs within the pores. The reduction cycling was performed until the total stability of the plasmon peak position and intensity in the case of hydroquinone was reached. This number of cycles was then fixed for syntheses with the other reducing agents for comparison (Figures 4 and S1 in the Supporting Information). One should note that the plasmon intensity evolution tends to be weakened after the fourth cycle.

The increase in size of the AuNPs with the number of reduction cycles was evidenced by high-resolution electron microscopy (Figure 5). On average, the AuNP diameter increased from 10 to 30 nm when the reduction cycles were repeated five times. Using FFT on these same TEM pictures, it was possible to analyze the AuNP crystalline structure, summarized in Table 2. A distance $d_{(111)}$ close to 0.235 nm was measured and attributed to the interplanar distance for the

(111) plane based on the literature.⁴¹ The lattice parameter could be calculated from these values and was found close to the lattice parameter of gold, $a = 0.407$ nm, which is in agreement with the previously reported studies on AuNPs.^{41,42} It is worth pointing out that the NP size evolution seen over these cycles seems to be mostly driven by the nature of the reducing agent.

2.1.3. Effect of the Reducing Agent. As mentioned above, the nature of the reducing agent drove the AuNP size. NaBH₄ has a stronger reducing power (*i.e.*, a more negative redox potential) than ascorbic acid and hydroquinone (Table 3). The observation of the plasmon resonance bands in Figure 4 shows the appearance of this plasmon resonance band after 2 cycles in the case of ascorbic acid and hydroquinone instead of just one in the case of NaBH₄. This underlines the ability of the latter to form proper seeds from the start instead of very small nuclei in the case of ascorbic acid or hydroquinone. It is worth noting that when using sodium citrate as a reducing agent, the reduction was quite ineffective. Sodium citrate is known to be a very weak reducing agent that can reduce Au(III) ions only to the Au(I) state.⁴³ The higher the reducing power, the more the nucleation was favored over the growth, resulting in better seeds in the early cycles and smaller final AuNPs.

As seen in Figure 6, SEM images assert that the reduction, after 5 reduction cycles with NaBH₄, ascorbic acid, or hydroquinone, occurred both on the surface and within the pores of all Au-containing membranes.

The AuNPs were nicely distributed inside the pores and aligned themselves along these channels. Their diameter (ϕ_{NP}), measured over 200 AuNPs, was found to be equal to 32 ± 6 nm, 29 ± 6 nm, and 44 ± 5 nm for NaBH₄, ascorbic acid, and hydroquinone, respectively.

High resolution TEM (HR-TEM) was performed by preparing ultrathin AuNP-containing P4VP-g-PVDF composite membrane sections made by ultramicrotomy. It enabled the

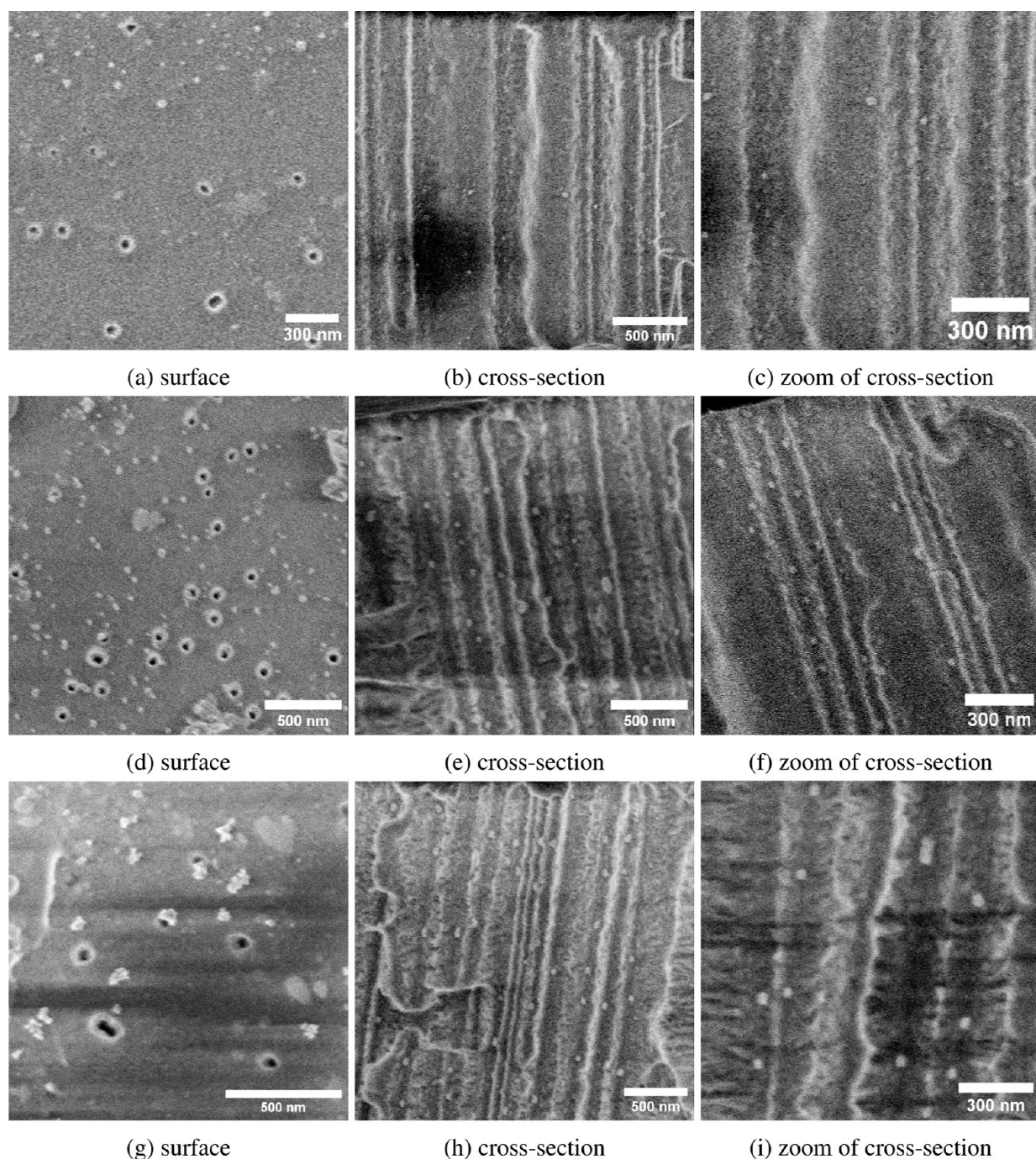


Figure 6. SEM images of Au-containing P4VP-g-PVDF membranes after 5 reduction cycles using (a–c) NaBH_4 , (d–f) ascorbic acid, and (g–i) hydroquinone.

acquisition of a series of HR-TEM images of the *in situ*-grown AuNPs present inside the core of P4VP-g-PVDF nanochannels. Figure 7a displays the reconstructed 2D map of the entire nanoporous composite thickness (see also Figures S2–S5 in Supporting Information for low magnification TEM images).

AuNPs have homogeneously grown without noticeable depth-related variations in size (Figure 7b). The average AuNP size measured by TEM was found to be similar to that determined by SEM. An Au elementary mapping was also performed on the NANOSCOPIUM beamline of the SOLEIL synchrotron, using space-resolved X-ray fluorescence (XRF) (resolution of 50 nm) on the whole area of a cross-section of the

AuNP-containing P4VP-g-PVDF membranes. These measurements confirmed the presence of gold along the whole nanopore length, as shown in Figure 8a. This Au composition was in agreement with the NPs observed within the nanopores by HR-TEM coupled with EDX mapping (Figure 8b).

In the specific case of reduction using hydroquinone, some AuNPs exhibited an elongated shape in the pore direction with an aspect ratio in the range of 1:2 to 1:4, as shown in Figure 9a. It was reported^{47,48} that hydroquinone may serve as a reducing agent in gold nanorod seeded-growth synthesis. However, the zoomed-in image of a specific elongated AuNP seemed to support the hypothesis of the ability of two or more AuNPs to

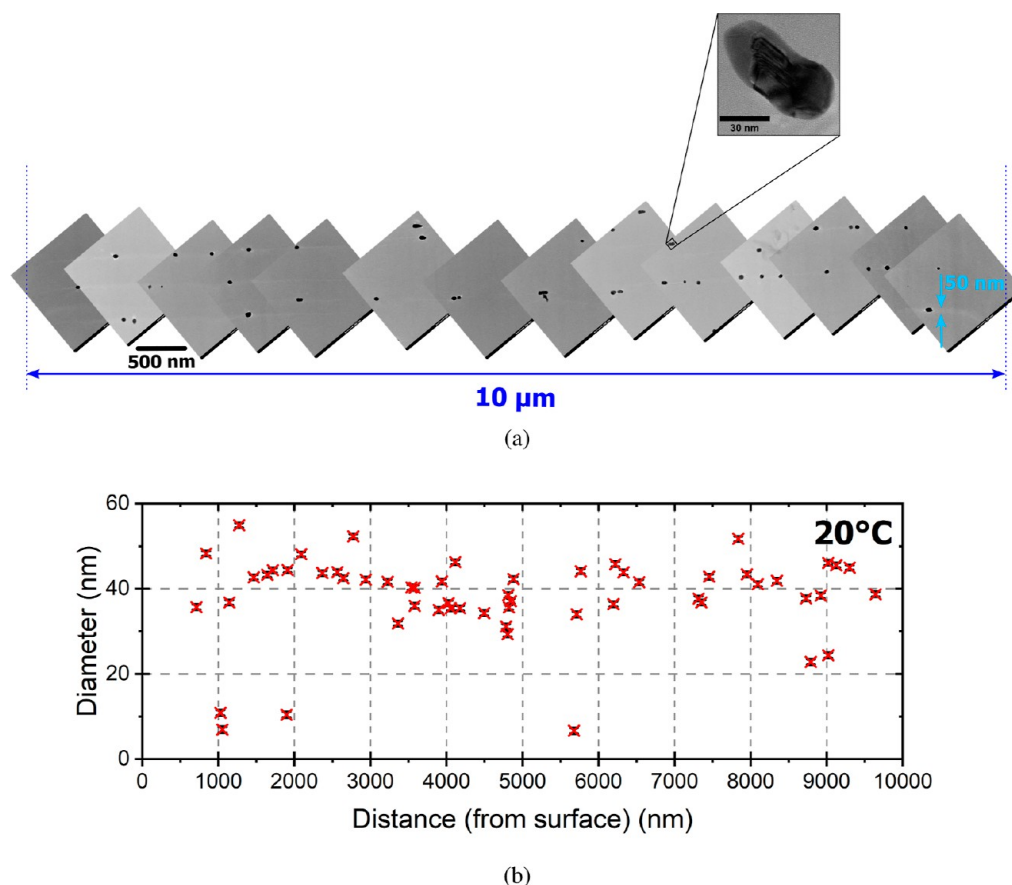


Figure 7. (a) Combination of TEM images for cross-section reconstruction of a P4VP-g-PVDF membrane containing AuNPs synthesized with 5 reduction cycles using hydroquinone as the reducing agent at room temperature (inset: HR-TEM of an AuNP); (b) corresponding distribution of AuNP sizes along the membrane thickness (made over the 60 AuNPs of the reconstructed cross-section).

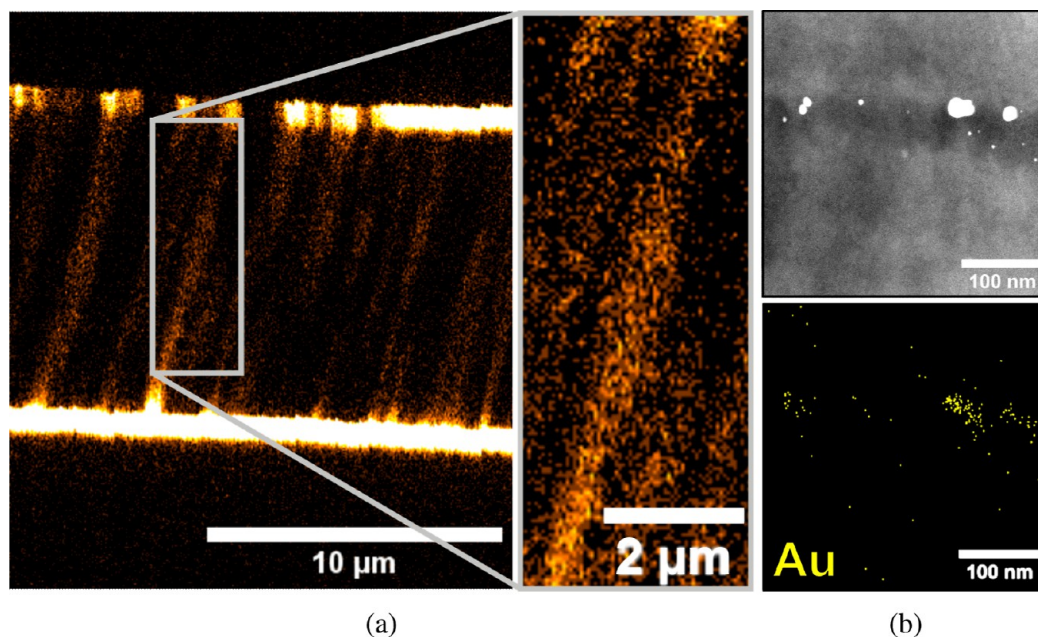


Figure 8. (a) Space-resolved (resolution 50 nm) XRF elementary mapping for gold of the cross-section of a AuNP-containing P4VP-g-PVDF membrane, with a zoomed-in image of a pore; (b) AuNPs inside the P4VP-g-PVDF membrane nanopores seen by (top) high-angle annular dark field (HAADF) imaging and (bottom) corresponding EDX mapping for the Au element.

merge together instead of the anisotropic growth of an individual AuNP. Indeed, the FFT on HR-TEM images (Figure

9b) strengthens this hypothesis by showing a monocrystalline domain right in the center of a polycrystalline elongated AuNP.

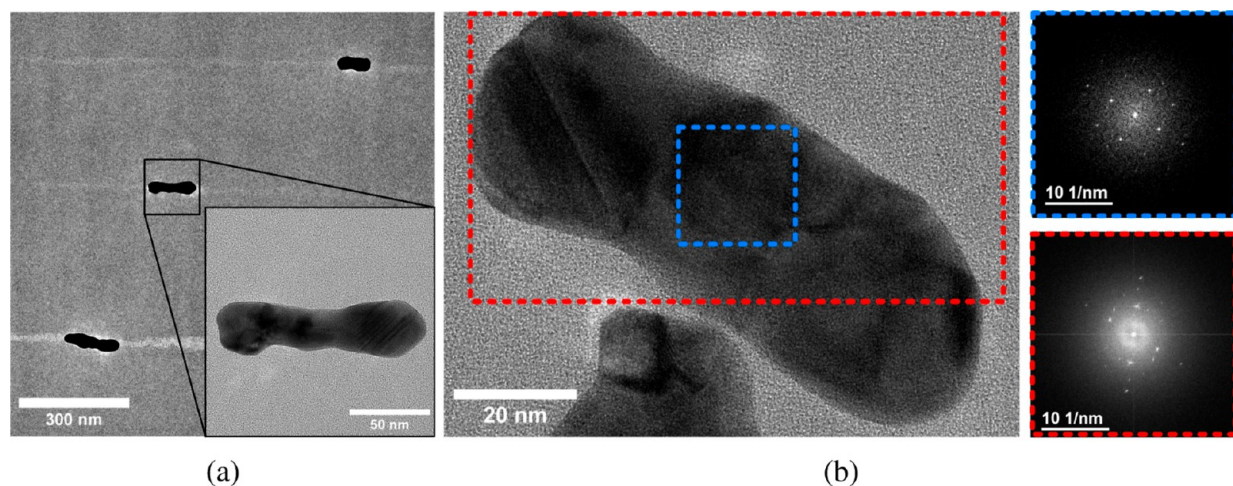


Figure 9. (a) TEM cross-section image of a Au-containing PVDF-P4VP membrane after 5 reduction cycles using hydroquinone as the reducing agent (with inset: zoom) showing the elongation of some AuNPs inside the nanopores; (b) TEM image at higher magnification on an elongated AuNP, with the corresponding FFT images for 2 sites (blue and red square areas).

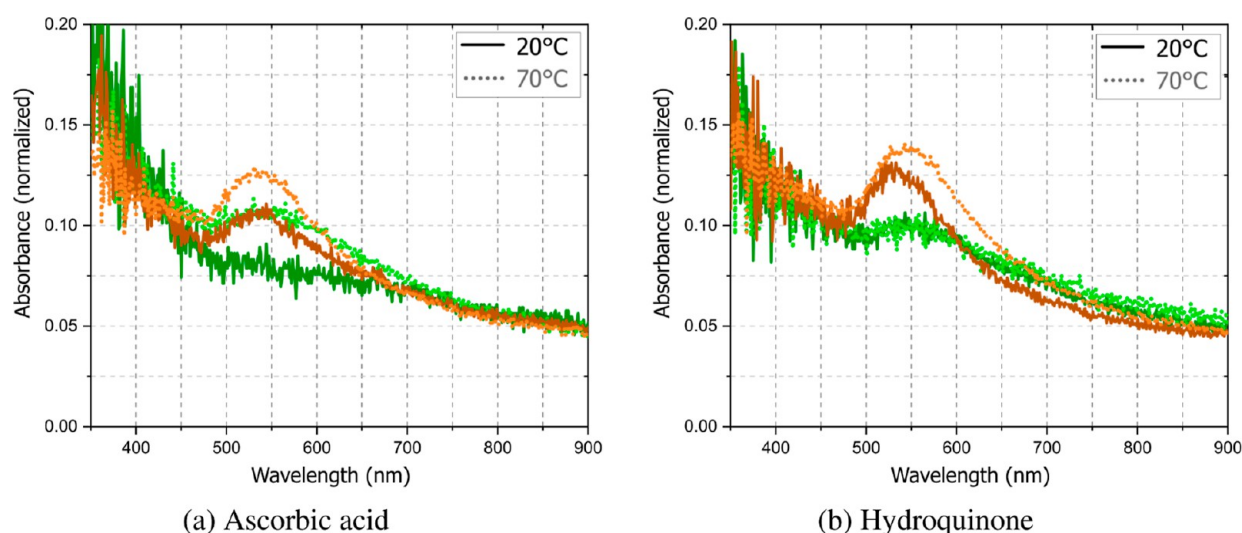


Figure 10. UV–visible spectra of the Au-containing P4VP-grafted PVDF membrane after 2 (green) and 4 (brown-orange) reduction cycles at 20 °C (solid lines) and 70 °C (dashed lines) using (a) ascorbic acid or (b) hydroquinone as a reducing agent.

The crystal lattice parameter of this monocrystalline domain, measured from the FFT, was determined at 0.413 nm, in accordance with values known for gold NPs.^{41,42} The presence of this polycrystallinity for the elongated AuNPs, composed of monocrystalline parts along the elongation axis, is consistent with the merging of various seeds grown into one unique AuNP. This phenomenon was not observed when the reduction occurred using NaBH₄ or ascorbic acid as reducing agents, for which the AuNP mean sizes were smaller. Since, in the case of the hydroquinone reduction synthesis, the mean AuNP size corresponded to the nanopore mean diameter, *i.e.*, 45 ± 6 nm, this AuNP elongation phenomenon suggests mostly a template effect in coherence with merged AuNP observations rather than a nanorod seeded-growth synthesis.

To bring energy to the system as a way to strengthen the reducing power (E^0) of the mild-reducing agents (sodium citrate, ascorbic acid, and hydroquinone) as predicted by the Nernst equation, the effect of heating on the growth of the AuNPs was investigated by performing the reduction step at two temperatures: 20 and 70 °C. Figure 10a shows that, in the case of

a reduction with ascorbic acid as a reducing agent, the obtained plasmon resonance band at 70 °C after only 2 cycles was as intense as the plasmon resonance band after 4 cycles at room temperature.

This temperature effect was also observed when hydroquinone was used as a reducing agent (Figure 10b), with a larger plasmon resonance bandwidth and red shift after 4 cycles, from 534 to 548 nm, corresponding to the formation of bigger AuNPs. These results underline the fact that the thermal energy brought to the system has favored the nanocrystal growth. When using hydroquinone at 70 °C, TEM measurements (Figure 11) indicated the polydispersity in AuNP size with two populations, one centered at 5 nm and a more dispersed one centered at 41 nm. These two populations were still homogeneously distributed within the membrane.

It is worth noting that, in that case, no elongated NPs were observed. As described in the Scheme 2, the assumption is that the energy uptake favors tremendously the nucleation events of the second population over the growth of the existing crystals, preventing them from merging.

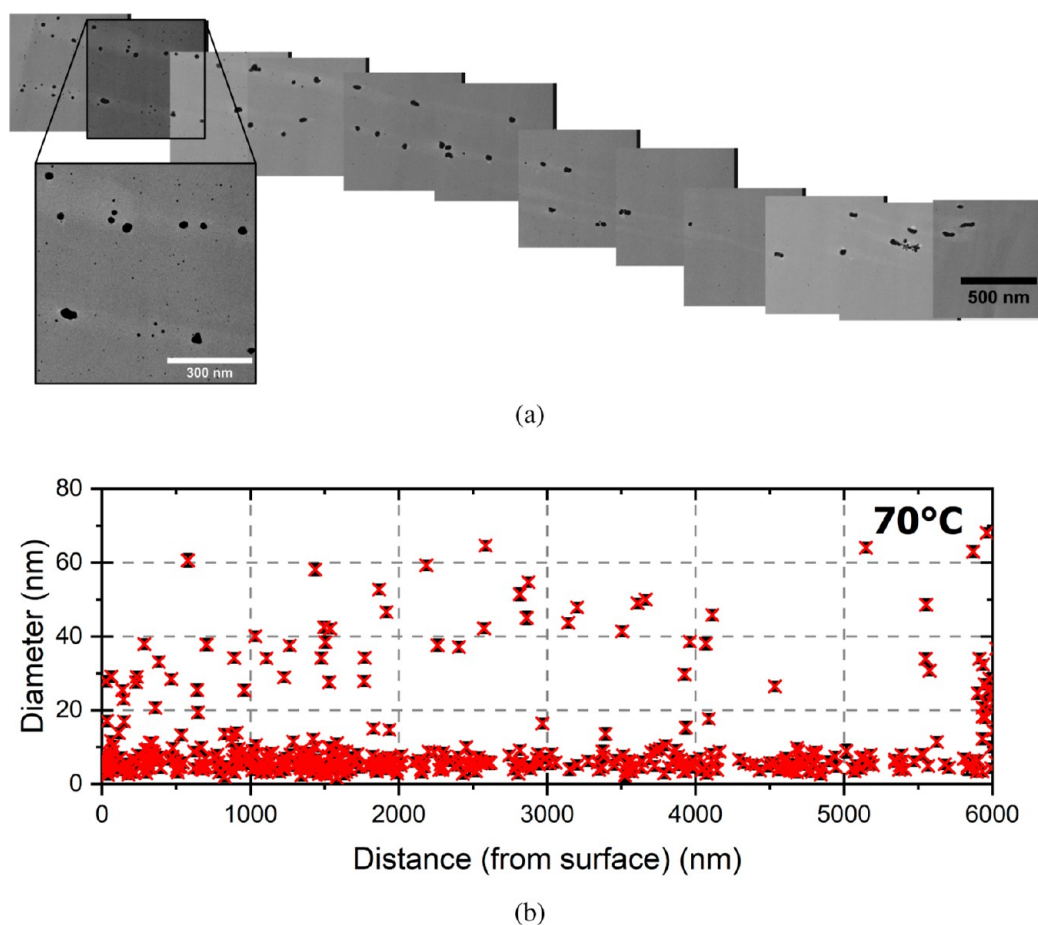
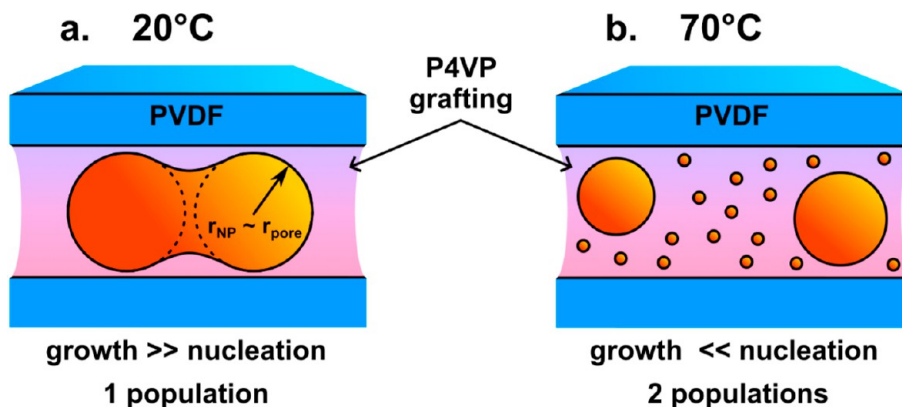


Figure 11. (a) Combination of TEM images for cross-section reconstruction of a P4VP-grafted PVDF membrane containing AuNPs synthesized with 5 reduction cycles using hydroquinone as the reducing agent at 70 °C; and (b) the corresponding size distribution of the AuNP diameter along the membrane thickness (made over 500 AuNPs). Two populations (5 and 41 nm) are clearly distinguishable.

Scheme 2. Description of the In Situ AuNP Growth Mechanisms after Reduction with Hydroquinone: (a) Merging of Two Neighboring AuNPs at 20 °C (Template-Assisted Growth); (b) Formation of a Secondary Population at 70 °C



For the specific case of sodium citrate, the addition of thermal energy allows a better reduction of Au(I) into Au⁰, enhancing the synthesis of AuNPs. As shown in Figure 12b, the plasmon due to the AuNPs in the nanocomposite P4VP-g-PVDF membranes prepared with 5 reduction cycles using sodium citrate at 70 °C was much more pronounced (colorful sample) than the one when the reduction was performed at 20 °C. Under these conditions, the average AuNP diameter was 31 ± 6 nm, similar to what was obtained with ascorbic acid at room temperature (Figure 13).

A summary of the specific features (plasmon resonance band wavelength, AuNP size) for all the Au-containing P4VP-g-PVDF membranes prepared with 5 reduction cycles is shown in Table 4. Pictures of the corresponding samples can be found in Figure S6 in Supporting Information. It is important to mention that the reduction using sodium citrate at room temperature was not very efficient in synthesizing the AuNPs; hence, the value of λ_{plasmon} was obtained from a weak band, and also the measurement of the AuNP mean diameter was made on very few AuNPs (less than 50 AuNPs).

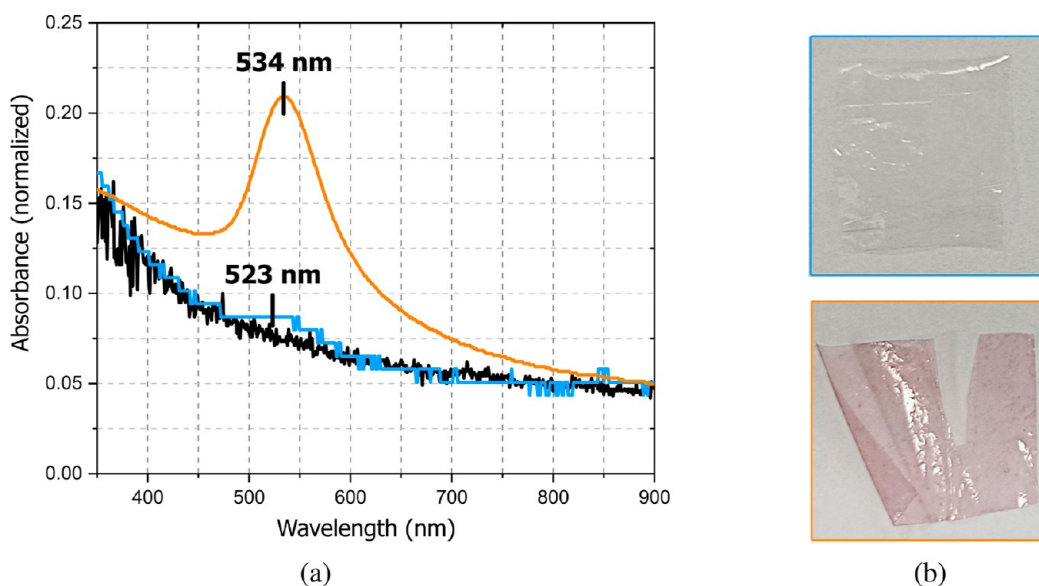


Figure 12. (a) UV–visible absorption spectra for P4VP-g-PVDF membranes (black) before and after synthesis of AuNPs with 5 cycles of reduction using sodium citrate at (blue) 20 °C and (orange) 70 °C; (b) color of these same membranes: reduction at (top) 20 °C and (bottom) 70 °C.

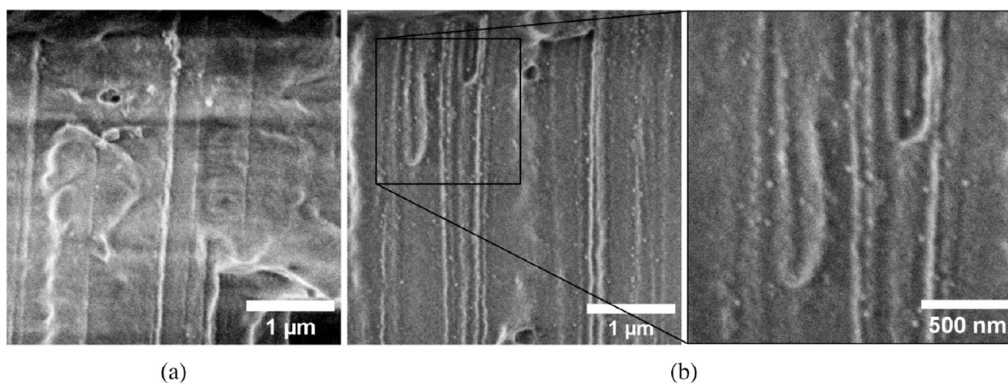


Figure 13. SEM pictures of the Au-containing P4VP-grafted PVDF membrane after 5 reduction cycles using sodium citrate as the reducing agent at (a) room temperature and (b) at 70 °C.

Table 4. Summary of the Plasmon Resonance Wavelength and AuNP Size (Measured from SEM Images on around 200 AuNPs) Depending on the Reducing Agent and Temperature Used for 5 Reduction Cycles Synthesis in P4VP-g-PVDF Membranes

reducing agent	sodium citrate		ascorbic acid		hydroquinone		NaBH ₄	
temperature (°C)	20	70	20	70	20	70	20	70
λ_{plasmon} (nm)	523	534	528	532	534	548	523	526
$\phi_{\text{NP}}^{\text{SEM}}$ (nm)	31 ± 8	31 ± 6	29 ± 6	39 ± 5	44 ± 5	41 ± 30 ^a 4 ± 5 ^a	32 ± 6	

^aTwo populations of different sizes were present.

2.2. Optical Properties of Nanoporous AuNP/P4VP-g-PVDF Composites

2.2.1. Spectroscopical Measurements. *In situ* growth of AuNPs within the polymer nanopores is expected to change the optical properties of the composite material.^{6,7,9} As already demonstrated, the AuNP plasmon resonance in the region 515–550 nm was more or less intense, depending on the reducing agent, the temperature, and the number of reduction cycles (Figure 4). As displayed in Figure 14, this absorption contribution was also present in the transmittance and reflectivity of the nanocomposite membrane. Note that in the case of the citrate-induced synthesis, the results were given for the synthesis at 70 °C since almost no AuNPs were formed at

room temperature with this reducing agent. The total reflectivity (including the specular and diffuse reflectivities) was almost unchanged (around 2%) by the growth of the AuNPs within the PVDF–P4VP membrane. This small effect of the plasmon absorption on the reflectivity was mostly driven by the diffuse reflectivity (Figure 14b). On another scale, the effect on the transmittance (Figure 14c) was found to be quite strong with a decrease of almost 25% at the plasmon resonance.

An interesting feature of plasmonic materials is illustrated in Figure 14d: the wavelength for the plasmon peak is shifted between the transmission and diffuse reflectivity spectra. This phenomenon, already well-documented⁴⁹ and whose most

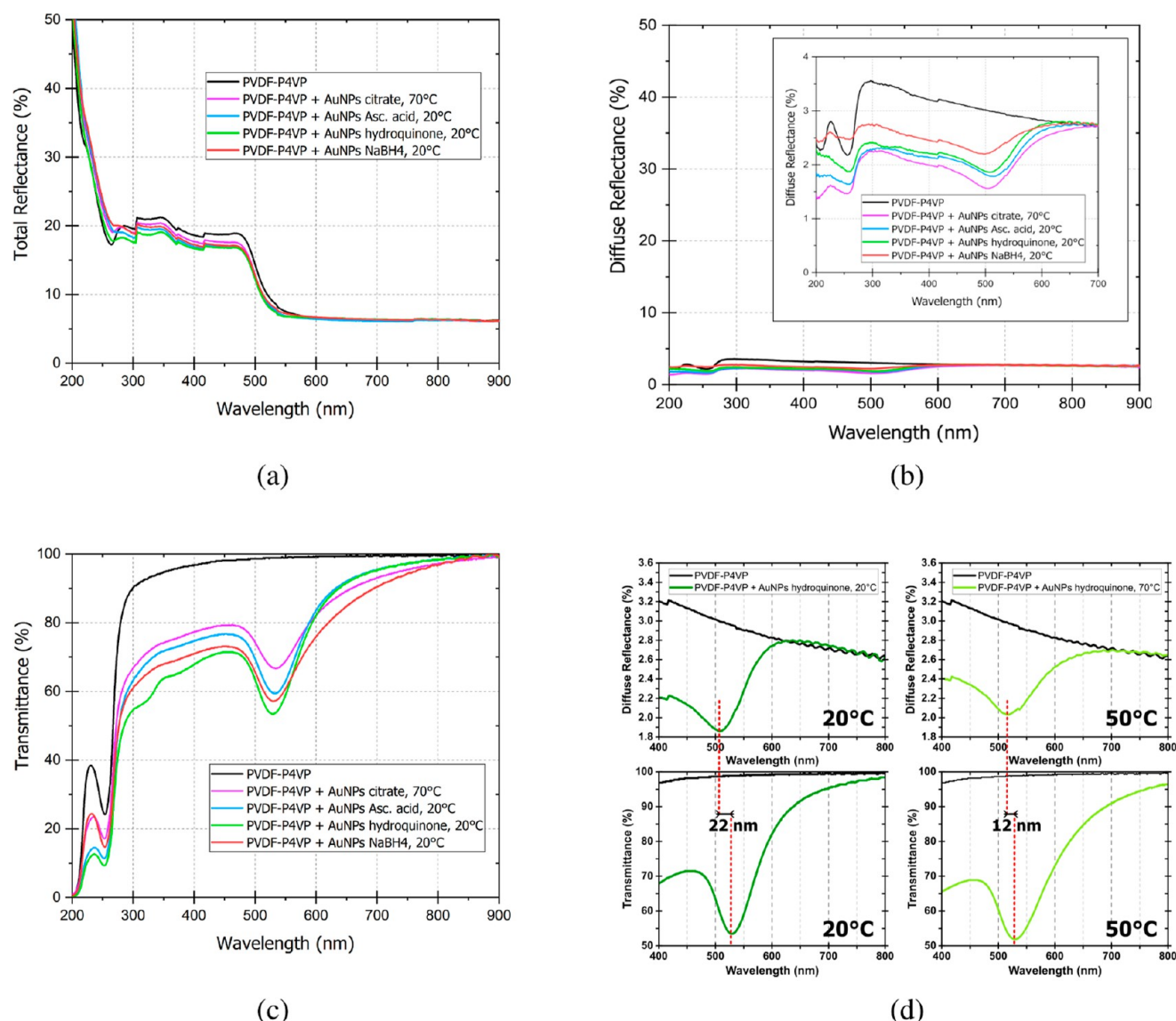


Figure 14. UV–visible (a) total reflectivity, (b) diffuse reflectivity (with zoom inset), and (c) transmission spectra for the AuNP-containing P4VP-g-PVDF membranes after 5 reduction cycles using the various reducing agents of this study; (d) specific transmission and diffuse reflectivity spectra in one case (hydroquinone) for both temperatures.

famous example is the Lycurgus cup,^{50,51} shows the whole potential of plasmon-based materials for optical applications.

2.2.2. Variation of the Refractive Index. Since the refractive index of air ($n_{\text{air}} = 1$) is smaller than that of the polymer ($n_{\text{PVDF}} = 1.42$), the inclusion of nanopores within the PVDF polymer membrane by ion-track etching is expected to first lower the refractive index of the whole material, according to the Lorenz–Lorentz eq (eq 1) for a binary system (a/b)⁵²

$$\frac{n_{\text{eff}}^2 - 1}{n_{\text{eff}}^2 + 2} = f_a \cdot \frac{n_a^2 - 1}{n_a^2 + 2} + f_b \cdot \frac{n_b^2 - 1}{n_b^2 + 2} \quad (1)$$

where n_{eff} is the effective refractive index of the material; n_a and n_b are the refractive indices of phases (a) and (b), for the PVDF and the air, respectively; and f_a and f_b are the volume fractions of these same phases.

The nanocomposite membranes in this study are ternary systems (polymer/air/gold); therefore, the Lorenz–Lorentz equation can be rewritten as eq 2

$$\frac{n_{\text{eff}}^2 - 1}{n_{\text{eff}}^2 + 2} = f_{\text{polymer}} \cdot \frac{n_{\text{polymer}}^2 - 1}{n_{\text{polymer}}^2 + 2} + f_{\text{air}} \cdot \frac{n_{\text{air}}^2 - 1}{n_{\text{air}}^2 + 2} + f_{\text{Au}} \cdot \frac{n_{\text{Au}}^2 - 1}{n_{\text{Au}}^2 + 2} \quad (2)$$

For simplification, and given the small amount of P4VP in these systems, the contribution of the radiografted P4VP onto the PVDF nanopores was not considered in the polymer phase, which was equal to the sole PVDF. Additionally, the air volume fraction was recalculated in order to take into account the filling with gold NPs, and the gold volume fraction was calculated from this filling value as well, so

$$f_{\text{air}}^{\text{real}} = f_{\text{air}} - \% \text{ pore filling} \cdot f_{\text{air}} \quad (3)$$

and

$$f_{\text{Au}} = \% \text{ pore filling} \cdot f_{\text{air}} \quad (4)$$

Combining eq 2 with this expression of the volume fraction for air (3) and gold (4), one can get the final expression for the composite refractive index

$$n_{\text{eff}}^2 = \frac{2 \cdot \left[f_{\text{polymer}} \cdot \frac{n_{\text{polymer}}^2 - 1}{n_{\text{polymer}}^2 + 2} + f_{\text{air}}^{\text{real}} \cdot \frac{n_{\text{air}}^2 - 1}{n_{\text{air}}^2 + 2} + f_{\text{Au}} \cdot \frac{n_{\text{Au}}^2 - 1}{n_{\text{Au}}^2 + 2} \right] + 1}{1 - f_{\text{polymer}} \cdot \frac{n_{\text{polymer}}^2 - 1}{n_{\text{polymer}}^2 + 2} + f_{\text{air}}^{\text{real}} \cdot \frac{n_{\text{air}}^2 - 1}{n_{\text{air}}^2 + 2} + f_{\text{Au}} \cdot \frac{n_{\text{Au}}^2 - 1}{n_{\text{Au}}^2 + 2}} \quad (5)$$

Given this new expression, the effective refractive index can be easily calculated for each AuNP-PVDF nanocomposite membrane. Figure 15 represents the evolution of this effective

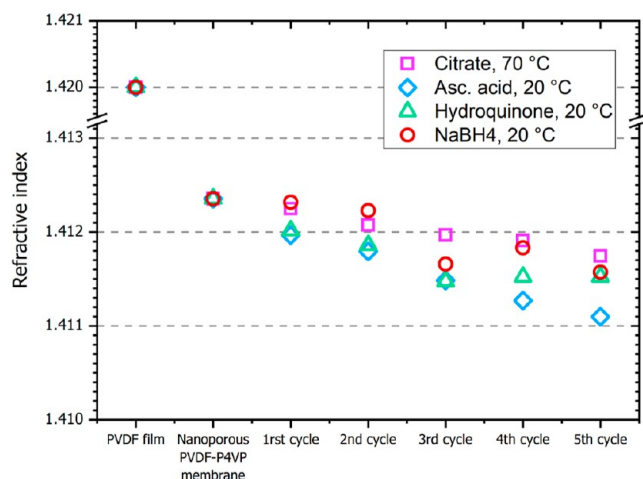


Figure 15. Evolution of the refractive index for the various nanocomposite membranes of this study, depending on the reducing agent and the number of reduction cycles operated during the synthesis.

refractive index over the reduction cycling for the various reducing agents. However, recent studies⁵³ have shown the importance of well defining the corresponding refractive index n_{Au} to use in the case of gold NPs. In a comparison of the determined refractive indices for Au layers with thicknesses from 10 to 41 nm, Shurvinton et al.⁵⁴ showed that the refractive index rapidly converges toward that of the bulk material (n_{Au} bulk taken from the Sopra SA database⁵⁵). As the present work deals with individual AuNPs (with sizes from 30 to 48 nm) and a plasmon band resonance around 530 nm, only refractive index values at the plasmon resonance band λ_{plasmon} were considered for calculation, i.e., n_{Au} was equal to 0.52^{53,54} for $\lambda_{\text{plasmon}} = 530$ nm. It is important to notice that these calculations are purely theoretical, only based on volume fractions, and no effect of the NP shape is taken into account.

The largest decrease ($n_{\text{PVDF}} = 1.42$ to $n_{\text{eff}} = 1.412$) is due to the introduction of porosity, i.e., introducing air in the materials, as it corresponds to a larger volume fraction than the AuNPs (1.5% of the membrane volume). The growth of AuNPs (corresponding only to a volume fraction of Au in the membrane around 0.2%) is observed in all cases with this decrease, although it is less pronounced. Reduction syntheses using ascorbic acid and hydroquinone seem to be the most effective ones for refractive-index lowering.

3. CONCLUSION

We have demonstrated an easy method to synthesize homogeneously distributed arrays of AuNPs directly within ion-track-etched nanoporous P4VP-g-PVDF membranes using a

simple protocol based on an immersion of the membrane into a gold salt precursor followed by a chemical reduction. Prior to reduction, the kinetics study of Au(III)-loaded nanopores has shown the efficiency of the P4VP polymer chains grafted onto the nanopore walls in complexing the Au(III) ions. Repetition of the loading/reduction cycles has proven to be an effective way to increase the size of the *in situ*-grown AuNPs, leading to well-defined AuNPs, homogeneously dispersed and aligned along the nanopores. It was also stated that the reducing power of the chemical reducing agent significantly affected the final size of AuNPs. Indeed, a strong reducing agent like NaBH_4 favors nucleation, leading to smaller AuNPs, while mild reducing agents, such as ascorbic acid or hydroquinone, favor growth toward bigger AuNPs. Furthermore, reduction with hydroquinone resulted in elongation of the AuNPs. Thanks to FFT HR-TEM image treatment, it was demonstrated that the elongated AuNPs resulted from the merging of several AuNPs. The proposed assumption is that, when the AuNP size becomes as big as the nanopore diameter, the host nanoporous membrane acts as a template, guiding the growth of gold between the AuNPs and leading to these elongated shapes.

Increasing the temperature during the reduction step favors the nucleation of gold nanocrystals. Even in the case of the very weak reducing agent, that is, sodium citrate, the heat boost enabled effective growth of the AuNPs. However, when dealing with the mild reducing agent, that is, hydroquinone, at 70 °C, the AuNP elongation was no longer observed. Instead, two size populations were formed, suggesting that nucleation was favored over the growth process. This counterintuitive result should be explained by diffusion limitation processes. Therefore, temperature-dependent kinetics studies are still required for further investigation.

It was also shown that the *in situ* growth of AuNPs within the transparent P4VP-g-PVDF membranes has led to modifications in the optical properties with a strong, tunable absorption around 530 nm due to the plasmon resonance, which was responsible for the change in the material color. Furthermore, variations in the effective refractive index of the nanoporous AuNP/P4VP-g-PVDF composites were calculated using the Lorenz–Lorentz equation adapted for the gold/air/polymer ternary system. It notably showed a decrease due to both the creation of nanoporosity and growth of the AuNPs within the polymer matrix. This decrease was remarkable even though the porosity fraction was quite low (2%) and the Au volume fraction was even lower (0.2%). This pioneering work has shown that it is possible to trigger elongation of AuNPs in a moderate aspect ratio (1:4 at maximum) through the template effect. Further experiments to tune both AuNP elongation and interparticle distance, as well as P4VP-g-PVDF pore density, could lead to more pronounced optical effects.

Nevertheless, the modulation of the absorption and the tuning of the refractive index of these nanocomposites turn them into interesting materials for optical applications (filters and sensors) and for the development of optical metamaterials.

4. EXPERIMENTAL SECTION

4.1. Chemicals

PVDF “Ajedum” films were purchased from the Solvay company. 4-Vinylpyridine (4VP; 95%), ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), gold(III) chloride trihydrate salt (HAuCl_4 ; >99.9%), hydroquinone (C_6H_4 -1,4-(OH)₂; extra pure), potassium hydroxide (KOH; ≥85%), potassium permanganate (KMnO_4 ; 97%), sodium borohydride (NaBH_4 ; ≥95%), and sodium citrate dihydrate ($\text{HOC}(\text{COONa})$ -

(CH₃COONa)₂·2H₂O; ≥99%) were purchased from Sigma-Aldrich. Sodium meta-bisulfite (Na₂S₂O₅; ≥95%) was purchased from Fluka.

4.2. Nanoporous P4VP-g-PVDF Membrane Synthesis

The synthesis of the nanoporous P4VP-g-PVDF membrane was performed following a protocol previously established in our group.¹⁶ PVDF films (with a thickness of $10 \pm 0.7 \mu\text{m}$) were irradiated using Swift Heavy Ion (SHI) at GANIL, France. The irradiation was carried out under the He atmosphere at room temperature either with ⁸⁶Kr³⁸⁺ at 10 MeV·mau⁻¹ or with ¹³⁶Xe^{43+/54+} at around 7 MeV·mau⁻¹, for a final fluence of 10⁹ ions·cm⁻². Irradiated PVDF films were conserved at -22 °C under a N₂ atmosphere.

Ion-track etching was then achieved by chemical attack at 65 °C in a mixture solution of KOH (10 M) and KMnO₄ (0.025 M) for 30 min, before being washed in sodium metabisulfite (15 ww %) and twice in deionized water. The average resulting pore diameter was measured as $45 \pm 6 \text{ nm}$ (over around 200 pores) from SEM images of ion-track-etched PVDF film surfaces, which is relevant for this etching time duration.¹⁶

Following the track-etching, P4VP radiografting was performed from the remaining radical on the surface of the pore walls. To do so, the track-etched membranes were immersed in vinylpyridine (95% purity, solution used as obtained from Sigma-Aldrich) in a sealed vial. The solution was then bubbled with N₂ for 15 min to eliminate all traces of oxygen, which may quench the remaining alkyl radicals in the ion-track-etched PVDF films. A reaction temperature of 65 °C was then set to thermally activate these radicals in order to initiate the radical polymerization of poly-4-vinylpyridine (P4VP) onto the pore walls. Afterward, the membranes were cleaned several times in deionized water and ethanol and finally put to equilibrate in a HCl solution (0.01 M) overnight. Then, the nanoporous P4VP-g-PVDF membranes were removed and let to dry gently at room temperature on a white absorbent paper.

4.3. In Situ Synthesis of AuNPs within the Membrane

The synthesis of AuNPs within the P4VP-grafted PVDF membranes was achieved in two steps. First, the membrane was immersed in an aqueous HAuCl₄ solution (0.01 M) under magnetic stirring for 1 h and then rinsed with deionized water. It was then immersed for 1 h under magnetic stirring in an aqueous solution of the selected reducing agent (0.01 M): ascorbic acid, hydroquinone, sodium borohydrate, or sodium citrate. Then, the membrane was rinsed with deionized water and dried. The reduction step was performed either at room temperature (around 20 °C) or at 70 °C.

These two steps of loading in HAuCl₄ and then reduction with the reducing agent can be repeated various times. In our study, 5 cycles were carried out when the effect of cycling was investigated.

4.4. Spectroscopy Characterization

UV–visible absorption analysis was performed on two spectrometers: a Unicam Thermo UV300, operating in the range 350–1100 nm; and a Shimadzu UV-2600i, equipped with an integrating sphere, operating in the range 190–1100 nm. In each case, the composite membranes were maintained on the beam pathway using a homemade 3D-printed magnetic sample holder.

4.5. Electron Microscopy Characterization

4.5.1. Scanning Electron Microscopy. Field emission scanning electron microscopy from Hitachi (S-4800 model) was used for the Au-containing PVDF–P4VP composite membrane imaging. Cross-section images were obtained by cryofracturing the composite membrane after immersion in liquid nitrogen for 5 min and then observing the sample using a 90°-tilt sample holder.

4.5.2. Transmission Electron Microscopy. High-resolution TEM was performed using a Themis 300 electron microscope, operating at an accelerating voltage of 300 kV. Thin resin-embedded cross-sections of the samples, prepared by ultramicrotomy, were deposited onto carbonated copper grids (300 mesh) for the TEM observation. In addition to imaging, energy-dispersive X-ray spectroscopy (EDX), integrated into the TEM system, was employed in HAADF imaging mode to determine the elemental composition of the

analyzed cross sections in the form of elementary maps of selected areas of the sample.

NP size distributions were determined from SEM and TEM images by manually measuring the NP diameters, using ImageJ software, over at least 200 NPs from several sites seen by microscopy. For the size distribution along the membrane thickness, the diameter was measured in the same way from the cross-sectional reconstitution of the P4VP-grafted PVDF AuNP-containing membrane for all the NPs seen in the TEM images.

4.5.3. Space-Resolved XRF on the NANOSCOPIUM Beamline.

Scanning X-ray fluorescence nanoimaging was performed at the NANOSCOPIUM hard X-ray nanoprobe beamline⁵⁶ of Synchrotron SOLEIL, France. A monochromatic 18.5 keV X-ray beam was obtained using a Si(111) double-crystal fixed-exit monochromator. To achieve a 70 nm (fwhm) spot size at the sample position, an achromatic nanofocusing Kirkpatrick-Baez (KB) mirror pair (JTEC) was employed. Sample alignment within the focal plane was facilitated by an extractable optical microscope placed between the KB mirrors and the sample. Two silicon drift diode detectors (SDD, VITUS H50, KETEK GmbH) were positioned symmetrically at ~75° to the incident beam to maximize the detection angle. The membrane was fixed on a sample holder mounted on a dual-stage scanning system: two stepper motors provided coarse scanning (0.5–1 μm pixel size), while a 2-axis piezo stage (P-561-3CD, Physik Instrumente) enabled high-resolution imaging (50 nm). All data were acquired using the FLYSCAN continuous scanning mode developed at Synchrotron SOLEIL, with a dwell time of 50 ms per 50 nm pixel. A full XRF spectrum was collected at each measurement point. The sum-spectra of the analyzed sample areas were fitted with the PyMCA software.⁵⁷ The elemental distribution maps of the elements identified from the sum-spectra were created by a homemade MATLAB.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.6c02970>.

Evolution of the plasmon peak intensity over the number of reduction cycles performed, for the AuNP-containing P4VP membranes prepared using NaBH₄, hydroquinone, and ascorbic acid as reducing agents; TEM cross-section images of a Au-containing PVDF–P4VP membrane after 5 reduction cycles using ascorbic acid as the reducing agent at (a) low, (b) medium and (c) high magnification; TEM cross-section images of a Au-containing PVDF–P4VP membrane after 5 reduction cycles using NABH₄ as the reducing agent at (a) low, (b) medium, and (c) high magnification; TEM cross-section images of a Au-containing PVDF–P4VP membrane after 5 reduction cycles using hydroquinone as the reducing agent at (a) low, (b) medium, and (c) high magnification. Zoomed-in image presented in (c) shows the elongation of some AuNPs, maybe due to the merging of two or more adjacent AuNPs into one; TEM images of a Au-containing PVDF–P4VP membrane after 5 reduction cycles using hydroquinone as the reducing agent at 70 °C at (a) low, (b) medium, and (c) high magnification; pictures of the various Au-containing PVDF–P4VP membranes after 5 reduction cycles using the various reducing agent of this study, at 20 °C and at 70 °C, and the Au-free reference PVDF–P4VP membrane on the top-left (PDF)

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Notes

The authors declare no competing financial interest.

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