

Electronic Supplementary Information

S.1. Literature review of NPs synthesis in Nafion.

Table S.1. Data regarding NPs synthesis in Nafion.

Nanoparticle type	Nanoparticle diameter (nm)	Reacting agent	Location	Reference
CdS	2-4	H ₂ S	uniform distribution	[1]
Pt	2.5	Heat treatment	uniform distribution	[2]
CdS	2.9	Thioacetamide	uniform distribution	[3]
TiO ₂	3.7 ± 0.5	Boiling H ₂ O	uniform distribution	[4]
CdS	4.1	Na ₂ S	surface	[3]
Pd	5 ± 1	NaBH ₄	uniform distribution	[5]
PbS	6.3 ± 1	Na ₂ S	uniform distribution	[6]
CdS	6.5 ± 1.2	Na ₂ S	uniform distribution	[6]
ZnO	8	Ethanol/NaOH	uniform distribution	[7]
Ag	9 ± 2	Formamide	uniform distribution	[8]
Ag ₂ S	10.5 ± 2.2	Na ₂ S	uniform distribution	[9]
Ag	13.0 ± 3.4	NaBH ₄	uniform distribution	[9]
Ag	13.4 ± 2.2	NaBH ₄	uniform distribution	[10]
Ag	15 ± 3	NaBH ₄	surface	[11]
Ag	15 ± 4	NaBH ₄	surface	[10]
CdS	ca. 1000	H ₂ S	uniform distribution	[12]

S.2. Nafion Pd-NPs

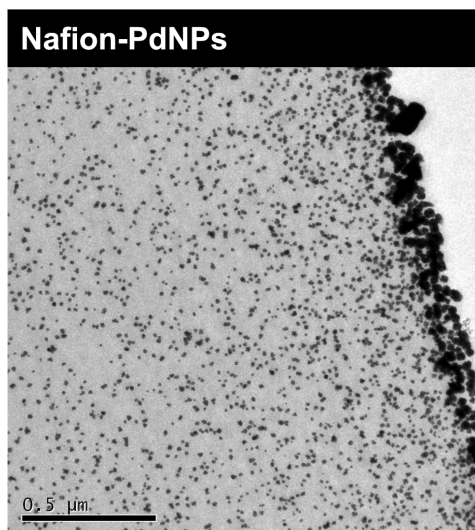


Figure S.2. TEM image of the cross-section of Nafion 117 with Pd-NPs.

S.3. Experimental.

S3.1. Materials

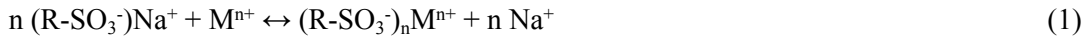
Nafion 117 membranes were from Sigma Aldrich, AgNO₃, NaBH₄, H₂SO₄ and H₂O₂ were all from Panreac and HNO₃ from Fisher Chemical.

S3.2. Nafion pretreatment

Commercial Nafion 117 membranes were washed twice with bidistilled water in an ultrasonic bath for 30 min. Then they were kept under stirring for 24 h in an aqueous oxidizing solution (10% of concentrated H₂SO₄ and 10% of commercial H₂O₂) to remove impurities. Afterwards, samples were washed again with boiling bidistilled water for several hours and kept in the fridge at 4 °C.

S3.3. Synthesis of AgNPs

The synthesis of MNPs in the membranes was carried out by a two-steps procedure, Intermatrix Synthesis (IMS) [13] (equations (1) and (2)), consisting in the loading of the ionogenic groups with the correspondent metal precursor (corresponding Mⁿ⁺ to Ag⁺ ions) and their subsequent chemical reduction by using NaBH₄ 0.5 M solution to obtain the metal nanoparticles (in this case, M⁰ stands for Ag⁰):



S3.4. Ultrasonic bath treatment

Samples of 1cm² were deposited in a closed vessel with 10 mL of bidistilled water and placed in an ultrasonic bath during different times: 30min, 60min, 120 min. Temperature of the bath during the experiment went up from 20 °C (initial temperature) to 40 °C (final temperature).

S3.5. Nanocomposite characterization

With the aim of characterizing the size and structure of the obtained MNPs, Transmission Electron Microscopy (TEM) was performed by a Jeol JEM-2011 HR-TEM and Jeol JEM-1400 TEM. FE-SEM images were obtained by a Zeiss Merlin, Carl Zeiss High Resolution SEM.

Before observation, samples were deposited between two plastic sheets in an epoxy resin and ultra-thin slices were obtained using an ultra-microtome and sputtered with Carbon.

Through the image analysis of TEM micrographs it was possible to make size distribution histograms from the sample data. By measuring the diameter of up to 600 AgNPs per sample, data were fitted to a 3-parameter Gaussian curve (3) where a is the height of Gaussian peak, d_m is the position of the center of the peak (corresponding to the most frequent diameter), and σ is the standard deviation.

$$y = a \cdot \exp \left[-0.5 \cdot \left(\frac{d - d_m}{\sigma} \right)^2 \right] \quad (3)$$

S3.6. Metal loading

The exact metal content in the prepared nanocomposites was analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7500). Samples of 1 cm² were digested with 1 mL of concentrated HNO₃ (65% w/w) overnight and then diluted 1:100 with distilled water. The resulting solutions (2 replicates) were appropriately diluted for ICP-MS analyses. After Ultrasonic bath treatment, the silver release was calculated as described previously [14].

S.4. FE-SEM characterization.

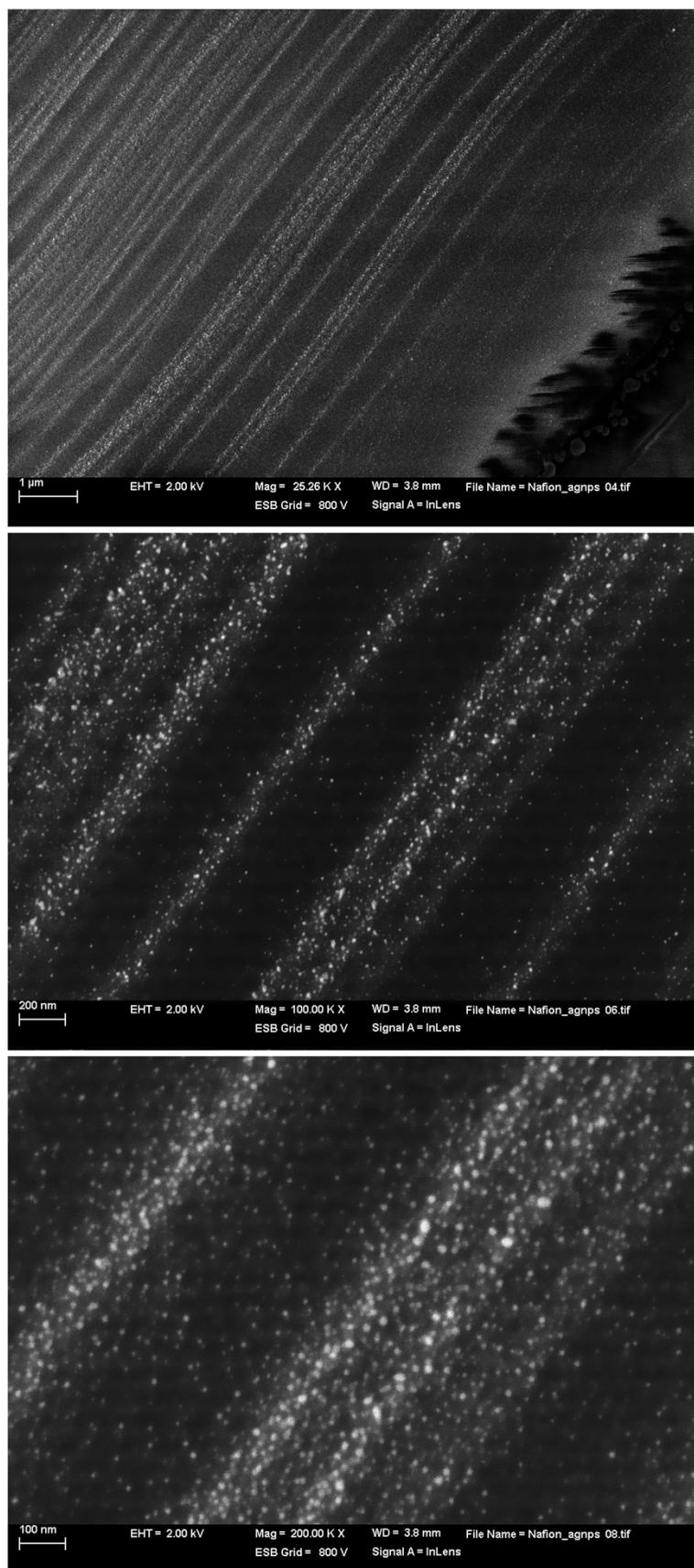


Figure S.4. FE-SEM images of the cross-section of Nafion 117 with AgNPs.

S.5. NPs size distribution.

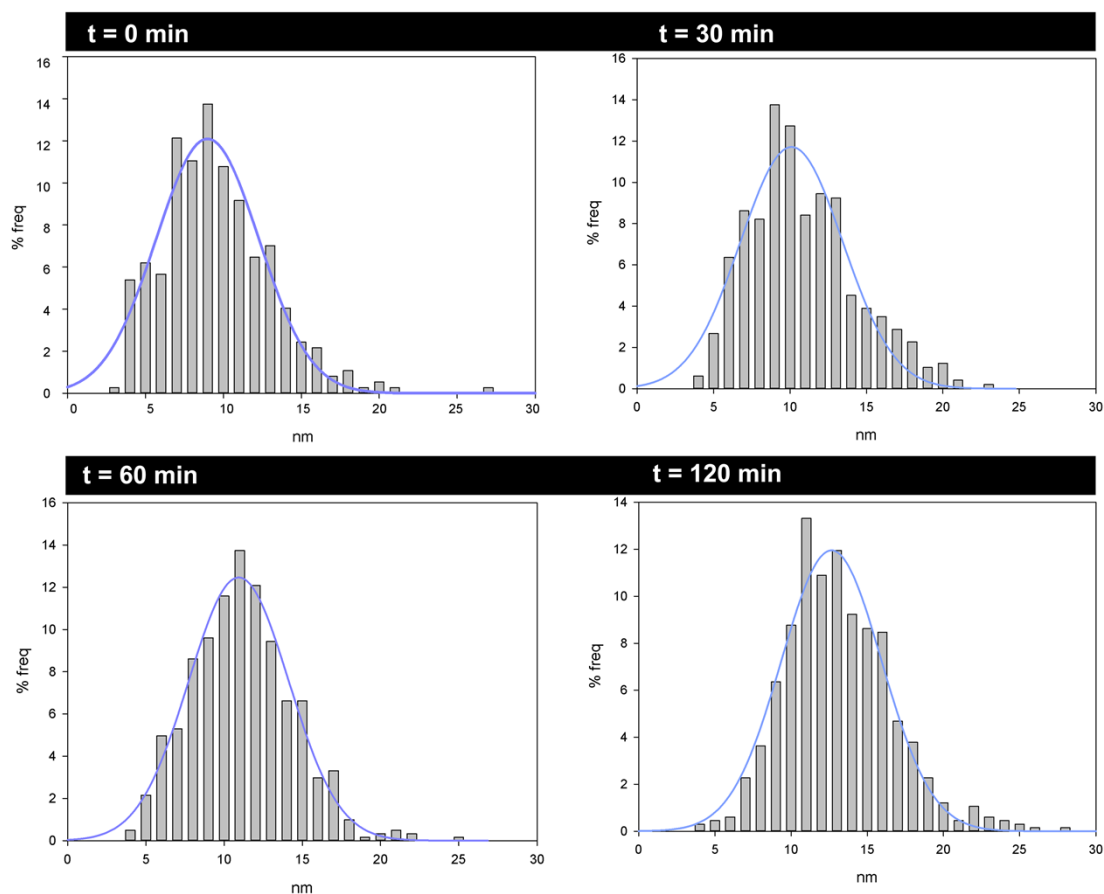


Figure S.5.1. Size distribution histograms of the nanocomposite samples after immersion in an ultrasonic bath for different times.

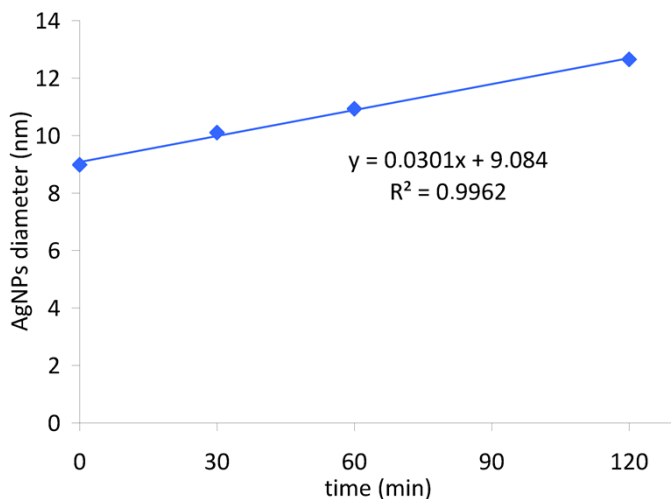


Figure S.5.2. Linear evolution of NPs diameter vs. time of the US treatment.

The Ag-NPs average diameter found for the original samples (without being treated by ultrasounds) was 9.0 ± 0.2 nm which is in close agreement with the water cavity size for a Nafion membrane extrapolated from data plotted in reference [15]. The content of water was considered 67 ± 6 g of water per 100 g of dry polymer form reference [16].

S.6. Schematic representation of hydrated Nafion

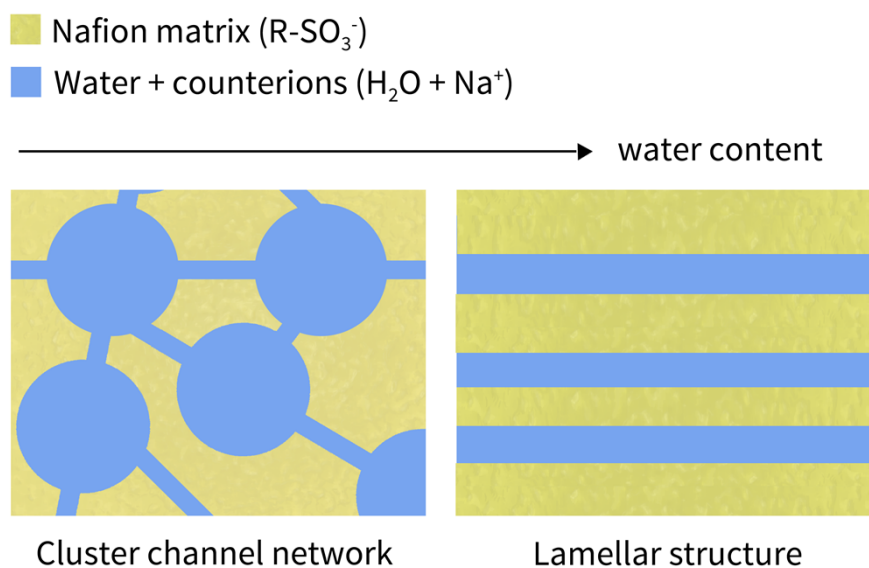


Figure S.6.1. Schematic representation of hydrated Nafion matrix.

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