

# ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## COMMUNICATION

## Uncommon patterns in Nafion films loaded with silver nanoparticles†

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012Berta Domènech<sup>a</sup>, Maria Muñoz<sup>a</sup>, Dmitri N. Muraviev<sup>a</sup> and Jorge Macanás<sup>\*b</sup>

DOI: 10.1039/x0xx00000x

www.rsc.org/

**Nafion has been frequently used for the synthesis of nanoparticles taking advantage of its so-called cluster-network structure. Unexpectedly, the synthesis of AgNPs inside Nafion 117 was found to produce NPs organization, following a regular pattern that can reveal the real morphology of the polymer.**

Nafion is a poly(perfluorosulfonic) acid membrane, known for its cation exchange properties as well as for its thermal and chemical stability.<sup>1</sup> It has been extensively used for a variety of applications<sup>2-4</sup>, and it is still the benchmark material against which most results are compared.<sup>4,5</sup> The chemical structure of Nafion-117 membrane consists of a polytetrafluoroethylene (PTFE) backbone and regularly spaced pendant side chain terminated by a sulfonate ionic group.<sup>2,5</sup> The unique behaviour of Nafion is explained by the lack of chemical cross-linking that provides a dynamic morphology,<sup>1,6</sup> responsible for phase segregation into hydrophilic and hydrophobic domains.<sup>7</sup>

Over the last 40 years many attempts have been carried out to precisely define chemical structure of Nafion. Although there have been several models under debate<sup>8,9</sup> (i.e. Fujimura's core-shell model, Dreyfus' local-order model, Haubold's sandwich-like model, Rubatat's rodlike model, Litt's lamellar model and Kreuer's film-like morphology), the pioneering cluster-network model proposed by Gierke et al.<sup>10</sup> is frequently reported in the literature for justifying Nafion properties, especially ion and water transport and ion permselectivity.<sup>1,11</sup> According to this model, polymer chains form reverse micelles in which sulfonate groups are lined in the wall encapsulating 4-5 nm water cavities connected by channels of ca. 10 Å in size.<sup>1,11</sup> However, nowadays there is quite an agreement regarding the inaccuracy of this model as it was based on the limited structure property information that was available at the time.<sup>4</sup>

Taking into account Gierke's model, those cavities defined by water clusters were suggested to be used as nanoscale reactors for the formation of nanoparticles (NPs). By this simple concept new composite materials can be prepared, in which the polymeric matrix controls the NPs size and avoids aggregation, preserving many of NPs special properties (i.e. catalytic and photocatalytic).<sup>12,13</sup> Accordingly, several studies were prompted for the synthesis of metal, metal oxides or metal sulphides NPs in such cavities.<sup>14-19</sup> Synthesis generally involved ion exchange of metal ions to the membrane matrix followed by a chemical reaction (i.e. reduction or

precipitation) producing NPs in the polymeric matrix. Still, very often the sizes of the formed NPs were much larger than the size of water clusters<sup>16-18</sup> (ESI† S1, Table S1). This paradox was sometimes rationalized in terms of additional hydration of ionic clusters or to polymer chain reorganization due to the incorporation of NPs. In addition to the NPs size disagreement, NPs location was not always consistent with a simple template procedure (ESI†, S1 Table S1).<sup>14,18</sup>

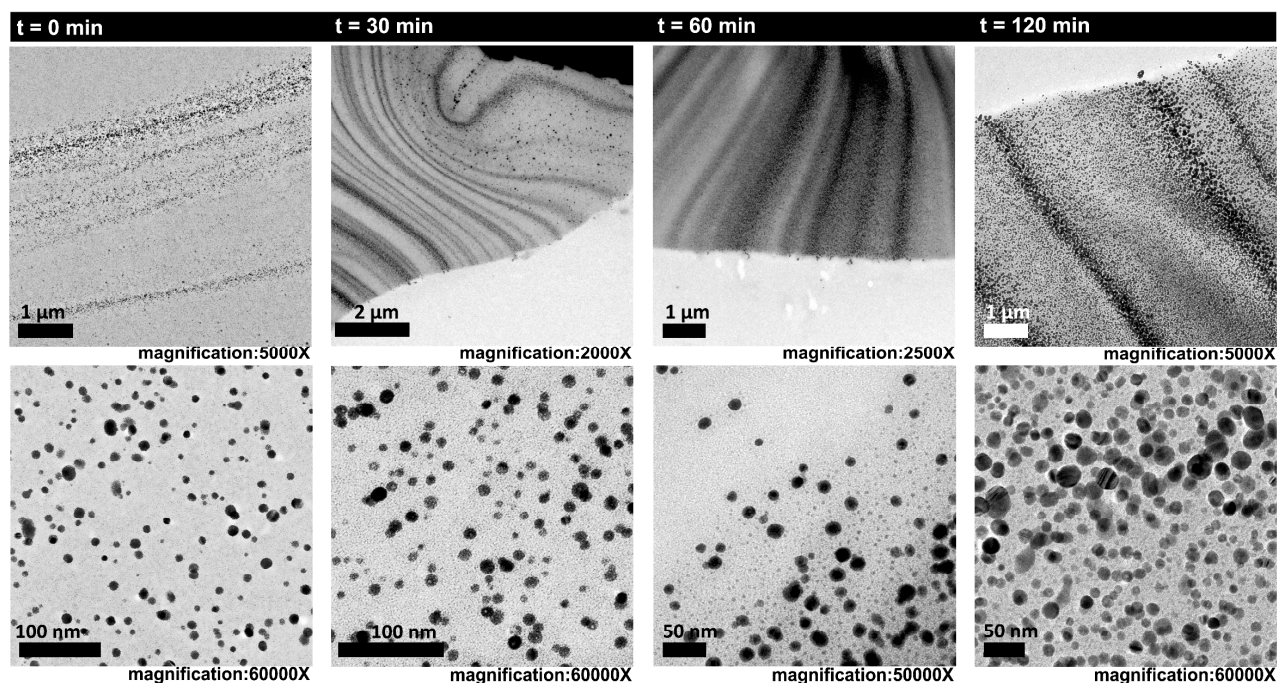
As a rule of thumb, it is generally accepted that anionic reagents (i.e.  $\text{BH}_4^-$ ,  $\text{S}^{2-}$ ) are repelled due to Donnan exclusion effect (DEE)<sup>20</sup> and NPs are formed on the surface of the polymer whereas neutral reagents (i.e. thioacetamide, formamide) or gases can freely diffuse through the matrix.<sup>16,21</sup>

Besides, the embedment of NPs can be regarded differently: the incorporation of NPs in the matrix can reveal the true morphology of the ionic channels of the membrane, behaving as a sort of nanometric staining agents. So, direct microscopy imaging of Nafion and related ionomer membranes embedded with nanoscale objects can provide new insight into the membrane structural domains and properties.<sup>18,22</sup>

In our previous works of intermatrix synthesis inside polymer films and resin beads<sup>23</sup>, NPs location was consistent with the DEE approach: NPs were mostly located on the surface of the samples, as it can be clearly seen in transmission electron microscopy (TEM) images of Nafion with Pd-NPs (ESI† S2, Fig. S2).<sup>13</sup> However, when carrying out the synthesis of Ag-NPs by a loading-reducing procedure (described in ESI† S3) and analysing the corresponding TEM images, it was revealed that the adjacent but not aggregated Ag-NPs followed a general pattern of almost parallel stripes (Fig. 1). In order to discard any artifact, samples were also analysed by high-resolution field emission scanning electron microscope (FE-SEM), giving the same result (ESI† S4, Fig. S4). Furthermore, when Ag-NPs-Nafion nanocomposites were introduced in an ultrasonic bath for different periods of time (ESI† S3), TEM images showed that stripes got coarser and more separated while the average diameter of Ag-NPs varied linearly with time (Fig. 2, ESI† S5, Fig. S5.1 and S5.2). Regarding the metal content, it was of 51.8 mg Ag/g dry membrane ( $s = 1.5$ ) for the as-prepared samples and almost constant after the ultrasonics treatment since Ag release was lower than 1% after 2 h.<sup>23c</sup>

At the best of our knowledge, this kind of images has never been published before for Nafion nanocomposites.

## COMMUNICATION



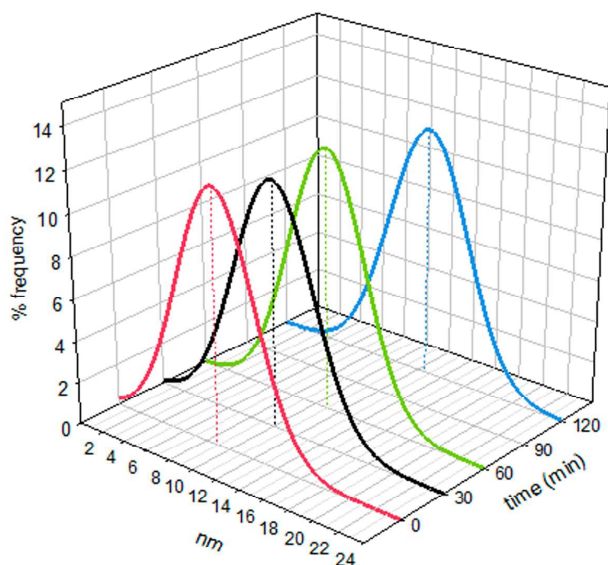
**Fig. 1.** Patterns observed for TEM images of Nafion samples containing Ag-NPs treated by ultrasounds at different times.

Though, these patterns occurring during materials deposition have been demonstrated experimentally for more than a century ago and are known as Liesegang rings (LRs) or bands.<sup>24,25</sup> LR's form when a soluble reactant (typically an ion) diffuses from the periphery of a medium (often a gel) uniformly filled with a second soluble reactant (typically another ion) to produce an insoluble substance. The gel medium would be the Nafion film loaded with  $\text{Ag}^+$  whilst  $\text{BH}_4^-$  would be the reactant that diffuses through.

In order to discern why such nanostructures were obtained, several factors were taken into account: i) Nafion structure; ii) membrane hydration and membrane pre-treatment; iii) reducing agent diffusion; iv)  $\text{Ag}^+$  mobility and v) ultrasound effect.

First, since the stripes are quite parallel instead of circular, the development of such LR-like bands would be in agreement with Litt's and Kreuer's models which describe Nafion as a multilayer structure where the ionic domains are defined as hydrophilic micelle layers separated by thin hydrophobic PTFE-like lamellar crystallites (ESI† S6, Fig. S6).<sup>4,9</sup> Swelling on the microscopic level should occur by having water incorporating between the lamellae, thereby pushing them farther apart what is a convenient and simple explanation for the swelling behaviour of Nafion as well as for the observed bands. Second, Moore and Martin<sup>26</sup> found that Nafion pre-treatment is crucial to define the polymer morphology since it rules the hydration state of the polymer and hydration controls the ions extent of penetration into the polymer.<sup>1</sup> Water uptake measurements showed that boiling in water clearly enhanced the ability of Nafion to absorb water when compared to the vacuum dried and as-received samples.

Third, it has been demonstrated by Pintauro et al.<sup>27</sup> that the aforementioned DEE explanation is oversimplified. They realized that anion transport through Nafion (previously boiled in water for 30 min) occurred efficiently for NaCl and the movement of  $\text{Cl}^-$  was thought to occur by co-ions moving together as a neutral particle, thus reducing the DEE.  $\text{Na}^+$  and  $\text{BH}_4^-$  can act similarly to  $\text{Na}^+$  and  $\text{Cl}^-$ , entering a fully hydrated region of the Nafion while single  $\text{BH}_4^-$  ions may experience limited transport. As a result, the feasibility to reduce metal ion precursors deep past the membrane surface might be hindered and the nucleation and growth of NPs occurs near this surface.<sup>21</sup> As well, the decomposition of  $\text{BH}_4^-$  produces  $\text{H}_2$ , which can diffuse freely through the membrane providing an additional autocatalytic reduction of  $\text{Ag}^+$  without any electrostatic repulsion.<sup>28</sup> Besides, it is worth to mention that Ag is one of the most attractive metal for nanomaterials synthesis and many different nanostructures have already been reported (i.e nanowires, nanoparticles, nanocubes).<sup>29</sup> This myriad of nanostructures testifies for Ag ability to undergo shape transformations by dissolution-precipitation processes even though the mechanisms are not fully understood.<sup>30</sup> Indeed, the mobility of ions inside Nafion 117 have been correlated to the membrane water-uptake<sup>6</sup> and  $\text{Ag}^+$  ions (which enhance water uptake) were found to possess a very high self-diffusion coefficient ( $1.61 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ), which provides them with a higher mobility when compared with other cations (i.e.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ). Then, it is not surprising that  $\text{Ag}^+$  ions were often associated with the formation of LR since their mobility aids in generating alternate regions of high and low concentration of the solid phase.



**Fig. 2.** Evolution of the distribution of nanoparticles diameter due to the duration of the ultrasounds treatment

Finally, it is well-known that ultrasounds offer a very attractive and fast method for the synthesis of metal NPs. Combining ultrasounds with classical Ostwald ripening<sup>31,32</sup> it is feasible that bigger nanocrystals grow at the expense of smaller ones that get dissolved. So, the growth of stripes can be a result of and induced dissolution-precipitation process. (Fig. 2, ESI† S5, Fig. S5.1 and S5.2).

## Conclusions

The simple concept of synthesising NPs by using Nafion's cavities ends up to be a much complex scenario that can give rise to uncommon patterned nanostructures as those shown here. But, even if the observed patterns have never been reported before for Nafion nanocomposites, their existence is in agreement with the general knowledge regarding reaction-diffusion mechanisms and reinforces the idea of hydrophilic-hydrophobic lamellar domains in Nafion.

## Notes and references

<sup>a</sup> Chemistry Department, Universitat Autònoma de Barcelona, UAB, 08193 Bellaterra, Barcelona, Spain.

<sup>b</sup> Department of Chemical Engineering, Universitat Politècnica de Catalunya, UPC, C/Colom, 1, 08222 Terrassa, Spain. Tel: +34 937398239; E-mail: jorge.macanas@upc.edu.

† Electronic Supplementary Information (ESI) available: [Experimental section, TEM and FESEM images, etc]. See DOI: 10.1039/c000000x/

- 1 A. Eisenberg and H.L. Yeager, Perfluorinated Ionomers Membrane, ACS Symposium Series 180, American Chemical Society, 1982.
- 2 C. Heitner-Wirguin, *J. Membr. Sci.* 1996, **120**, 1.
- 3 (a) V. Neburchilov, J. Martin, H. Wang and J. Zhang, *J. Power Sources*, 2007, **169**, 221; (b) C.J. Hora and D.E. Maloney, *Electrochem. Soc. Ext. Abstr.*, 1977, **77**, 1145.
- 4 K. Mauritz and R. Moore, *Chem. Rev.*, 2004, **104**, 4535.
- 5 H. Strathmann, Ion-exchange membrane separation processes, in: *Membrane Science and Technology*, Series 9, Elsevier, 2004, pp. 1.

- 6 A. Goswami, A. Acharya, and A.K. Pandey, *J. Phys. Chem. B*, 2001, **105**, 9196.
- 7 J. Chou, E.W. McFarland and H. Metiu, *J. Phys. Chem. B*, 2005, **109**, 3252.
- 8 (a) M. Fujimura, T. Hashimoto and H. Kawai, *Macromolecules* 1981, **14**, 1309; (b) B. Dreyfus, G. Gebel, P. Aldebert, M. Pineri, M. Escoubes and M. Thomas, *J. Phys. (Paris)* 1990, **51**, 1341; (c) G. Gebel and J. Lambard, *Macromolecules*, 1997, **30**, 7914; (d) H.G. Haubold, T. Vad, H. Jungbluth and P. Hiller, *Electrochim. Acta*, 2001, **46**, 1559; (e) L. Rubatat, A. Rollet, G. Gebel and O. Diat, *Macromolecules*, 2002, **35**, 4050.
- 9 (a) M.H. Litt, *Polym. Prepr.* 1997, **38**, 80. (b) K.D. Kreuer and G. Portale, *Adv. Funct. Mater.* 2013, **23**, 5390.
- 10 W.Y. Hsu and T.D. Gierke, *Macromolecules*, 1982, **15**, 101.
- 11 (a) W.Y. Hsu and T.D. Gierke, *J. Membr. Sci.*, 1983, **13**, 307; (b) T.D. Gierke, G.E. Munn and F.C. Wilson, *J. Polym. Sci. Polym. Phys. Ed.*, 1981, **19**, 1687.
- 12 N. Kakuta, J.M. White, A. Campion, A.J. Bard, M.A. Fox and S.E. Webber, *J. Phys. Chem.*, 1985, **89**, 48.
- 13 B. Domenech, M. Muñoz, D.N. Muraviev and J. Macanás, *Catal. Today*, 2012, **193**, 158.
- 14 P. Bertoncello, M. Peruffo and P.R. Unwin, *Chem. Commun.*, 2007, 1597.
- 15 (a) E.S. Smotkin, R.M. Brown, L.K. Radenburg, K. Salomon, A.J. Bard, A. Campion, M.A. Fox, T.E. Mallouk, S.E. Webber and J.M. White, *J. Phys. Chem.*, 1990, **94**, 7543; (b) Y. Zhang, D. Kang, C. Saquing, M. Aindow and C. Erkey, *Ind. Eng. Chem. Res.*, 2005, **44**, 4161; (c) P. Liu, J. Bandara, Y. Lin, D. Elgin, L.F. Allard and Y.-P. Sun, *Langmuir*, 2002, **18**, 10389; (d) N.H. Jalani, K. Dunn and R. Datta, *Electrochim. Acta*, 2005, **51**, 553.
- 16 (a) J. Wang, P. Liu, S. Wang, W. Han, X. Wang and X. Fu, *J. Molecular Catal. A: Chemical*, 2007, **273**, 21; (b) S. Wang, P. Liu, X. Wang and X. Fu, *Langmuir*, 2005, **21**, 11969.
- 17 (a) M. Krishnan, J.R. White, M.A. Fox and A.J. Bard, *J. Am. Chem. Soc.*, 1983, **105**, 7002; (b) R. Kumar, A.K. Pandey, S. Das, S. Dhara, N.L. Misra, R. Shukla, A.K. Tyagi, S.V. Ramagiri, J.R. Bellare and A. Goswami, *Chem. Commun.*, 2010, **46**, 6371.
- 18 (a) H.W. Rollins, F. Lin, J. Johnson, J.J. Ma, J.T. Liu, M.H. Tu, D.D. DesMarteau, and Y.-P. Sun, *Langmuir*, 2000, **16**, 8031; (b) Y.-P. Sun, P. Atornigijawat, Y. Lin, P. Liu, P. Pathak, J. Bandara, D. Elgin and M. Zhang, *J. Membr. Sci.*, 2004, **245**, 211; (c) H.W. Rollins, T. Whiteside, G.J. Shafer, J.J. Ma, M.H. Tu, J.T. Liu, D.D. DesMarteau and Y.-P. Sun, *J. Mater. Chem.*, 2000, **10**, 2081.
- 19 A. Sachdeva, S. Sodaye, A.K. Pandey and A. Goswami, *Anal. Chem.*, 2006, **78**, 7169.
- 20 F.G. Donnan, *J. Membr. Sci.*, 1995, **100**, 45.
- 21 A. Sode, N.J.C. Ingle, M. McCormick, D. Bizzotto, E. Gyenge, S. Ye, S. Knights and D.P. Wilkinson, *J. Membr. Sci.*, 2011, **376**, 162.
- 22 W. Kubo, K. Yamauchi, K. Kumagai, M. Kumagai, K. Ojima and K. Yamada, *J. Phys. Chem. C*, 2010, **114**, 2370.
- 23 (a) P. Ruiz, M. Muñoz, J. Macanás, C. Turtra, D. Prodius and D.N. Muraviev, *Dalton Trans.*, 2010, **39**, 1751; (b) J. Bastos-Arrieta, A. Shafir, A. Alonso, M. Muñoz, J. Macanás and D.N. Muraviev, *Catal. Today*, 2012, **193**, 207. (c) B. Domènech, N. Vigués, J. Mas, M. Muñoz, D.N. Muraviev and J. Macanás, *Solvent Extr. Ion Exc.* DOI: 10.1080/07366299.2013.839192.
- 24 (a) R.E. Liesegang, *Naturwiss. Wochenschr.* 1896, **11**, 353; (b) H.K. Henisch, Crystals in gels and Liesegang rings; Cambridge University Press: Cambridge, MA, 1988.
- 25 (a) D.A. Smith, *J. Chem. Phys.*, 1984, **81**, 3102; (b) M.I. Lebedeva, D.G. Vlachos and M. Tsapatsis, *Ind. Eng. Chem. Res.*, 2004, **43**, 3073.
- 26 R.B. Moore and C.R. Martin, *Macromolecules*, 1988, **21**, 1334.
- 27 P. Pintauro and D. Bennion, *Ind. Eng. Chem. Fundam.*, 1984, **23**, 234.
- 28 H. Lee, S.E. Habas, S. Kwekin, D. Butcher, G.A. Somorjai and P. Yang, *Angew. Chem. Int. Ed.*, 2006, **45**, 7824.
- 29 D. Muñoz-Rojas, J. Oró-Solé and P. Gómez-Romero, *J. Phys. Chem. C*, 2008, **112**, 20312 and references therein.
- 30 B.Y. Sun, B. Mayers, Y. Xia, *Adv. Mater.*, 2003, **15**, 641.
- 31 J.E. Park, M. Atobe and T. Fuchigami, *Electrochim. Acta*, 2005, **51**, 849.
- 32 R. Boistelle, and J.P. Astier, *Cryst. Growth*, 1988, **90**, 14.