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Uncommon patterns in Nafion films loaded with silver nanoparticles†

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Nafion has been frequently used for the synthesis of nanoparticles by taking advantage of its so-called cluster-network structure. Unexpectedly, the synthesis of AgNPs inside Nafion 117 was found to produce NPs organization, resulting in a regular pattern that could 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.[1] It has been extensively used for a variety of applications,[2–4] and it is still the benchmark material against which most results are compared.[4,5] The chemical structure of the Nafion-117 membrane consists of a polytetrafluoroethylene (PTFE) backbone and a regularly spaced pendant side chain terminated by a sulfonate ionic group.[2,5] The unique behaviour of Nafion is explained by the lack of chemical cross-linking that provides a dynamic morphology,[1,6] which is responsible for phase segregation into hydrophilic and hydrophobic domains.[7]

Over the last 40 years many attempts have been made to precisely define the chemical structure of Nafion. Although there have been several models under debate[8,9] (*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.*[10] is frequently reported in the literature for justifying Nafion properties, especially ion and water transport and ion permselectivity.[1,11] 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 size.[1,11] However, nowadays there is quite an agreement regarding the inaccuracy of this model as it is based on the limited structure property information that was available at the time.[4]

Taking into account Gierke's model, cavities defined by water clusters were suggested for use as nanoscale reactors in the formation of nanoparticles (NPs). Using this simple concept new composite materials can be prepared, in which the polymeric matrix controls the NPs size and avoids aggregation, preserving many of their special properties (*i.e.* catalytic and photocatalytic).[12,13] Accordingly, several studies were prompted for the synthesis of metal, metal oxide or metal sulphide NPs in such cavities.[14–19] Synthesis generally involved ion exchange of metal ions in 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[16–18] (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, the NPs location was not always consistent with a simple template procedure (ESI,† S1, Table S1).[14,18] As a rule of thumb, it is generally accepted that anionic reagents (*i.e.* BH_4^-, S^{2-}) are repelled due to the Donnan exclusion effect (DEE)[20] 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.[16,21]

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 agent. 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.[18,22]

In our previous reports of intermatrix synthesis inside polymer films and resin beads,[23] the NPs location was consistent with the DEE approach: NPs were mostly located on the surface of the samples, as can be clearly seen in transmission electron microscopy (TEM) images of Nafion with Pd-NPs (ESI,† S2, Fig. S2).[13] However, when carrying out the synthesis of Ag-NPs using 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

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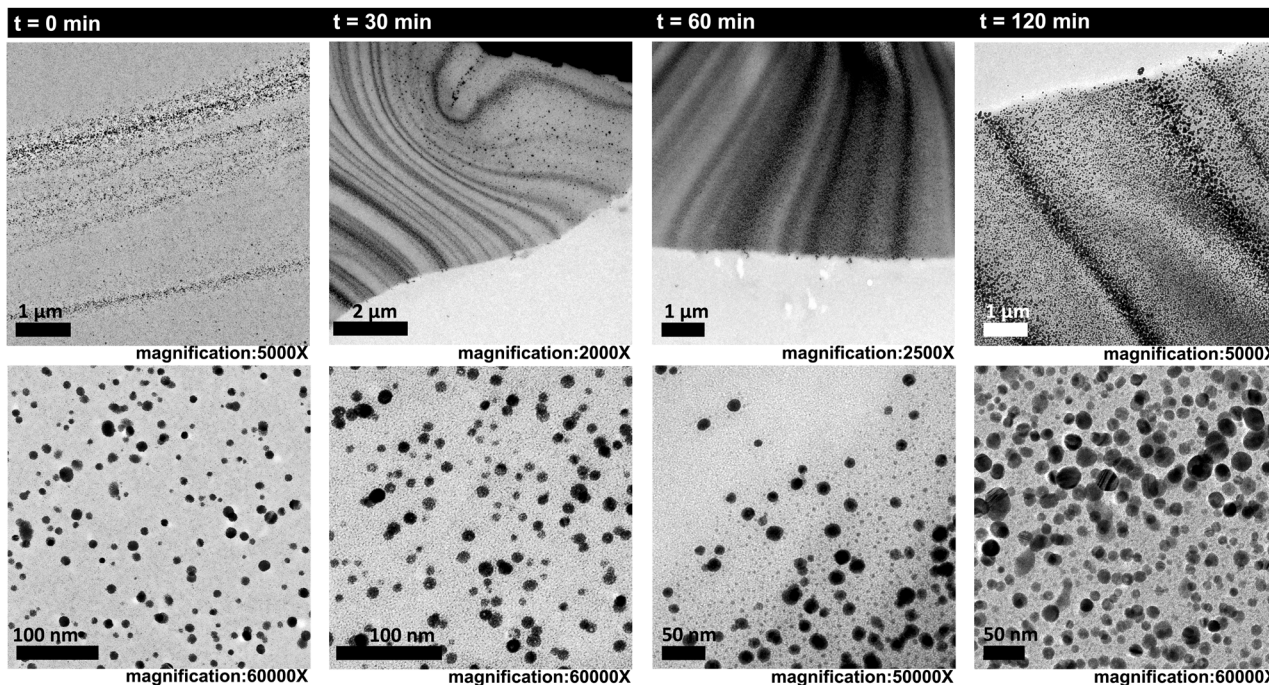
Fig. 1 Patterns observed of TEM images for Nafion samples containing Ag-NPs treated by ultrasound at different times.

parallel stripes (Fig. 1). In order to discard any artifact, samples were also analysed by high-resolution field emission scanning electron microscopy (FE-SEM), giving the same results (ESI,† S4, Fig. S4). Furthermore, when Ag-NPs-Nafion nanocomposites were introduced into an ultrasonic bath for different periods of time (ESI,† S3), TEM images showed that the 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 51.8 mg Ag g^{-1} dry
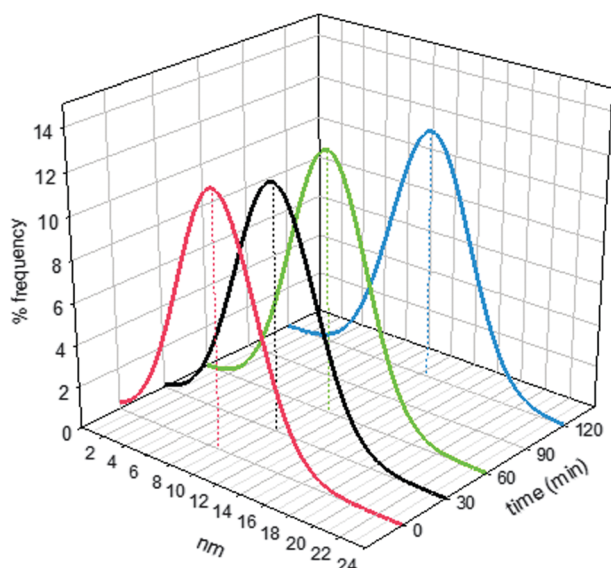

Fig. 2 Evolution of the distribution of nanoparticles diameter due to the duration of the ultrasound treatment.

membrane (s = 1.5) for the as-prepared samples and almost constant after the ultrasound treatment since Ag release was lower than 1% after 2 h.[23c]

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

However, these patterns occurring during material deposition have been demonstrated experimentally more than a century ago and are known as Liesegang rings (LRs) or bands.[24,25] LRs 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 Ag$^+$ whilst 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) the Nafion structure; (ii) membrane hydration and membrane pre-treatment; (iii) reducing agent diffusion; (iv) Ag$^+$ mobility and (v) ultrasound effects.

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 multilayered structure in which the ionic domains are defined as hydrophilic micelle layers separated by thin hydrophobic PTFE-like lamellar crystallites (ESI,† S6, Fig. S6).[4,9] Swelling of the microscopic level should occur by having water incorporation between the lamellae, thereby pushing them farther apart, which is a convenient and simple explanation for the swelling behaviour of Nafion as well as for the observed bands.

Second, Moore and Martin[26] 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 extent of penetration of the ions into the polymer.[1] 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.[27] 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 Cl$^-$ was thought to occur by co-ions moving together as a neutral particle, thus reducing the DEE. Na$^+$ and BH$_4^-$ can act similarly to Na$^+$ and Cl$^-$, entering a fully hydrated region of the Nafion while single BH$_4^-$ ions may experience limited transport. As a result, the feasibility of reducing metal ion precursors deeply past the membrane surface might be hindered and the nucleation and growth of NPs occurs near this surface.[21] As well, the decomposition of BH$_4^-$ produces H$_2$, which can diffuse freely through the membrane providing additional autocatalytic reduction of Ag$^+$ without any electrostatic repulsion.[28]

Besides, it is worth mentioning that Ag is one of the most attractive metals for nanomaterial synthesis and many different nanostructures have already been reported (i.e. nanowires, nanoparticles, nanocubes).[29] This myriad of nanostructures testifies to the ability of Ag to undergo shape transformations by dissolution–precipitation processes even though the mechanisms are not fully understood.[30] Indeed, the mobility of ions inside Nafion 117 have been correlated with the membrane water-uptake[6] and Ag$^+$ ions (which enhance water uptake) were found to possess a very high self-diffusion coefficient (1.61×10^{-6} cm^2 s^{-1}), which provides them with a higher mobility when compared with other cations (i.e. Na$^+$, K$^+$, Ca^{2+}). Then, it is not surprising that Ag$^+$ ions were often associated with the formation of LR since their mobility aids in generating alternating regions of high and low concentration of the solid phase.

Finally, it is well-known that ultrasound offer a very attractive and fast method for the synthesis of metal NPs. Combining ultrasound with classical Ostwald ripening[31,32] 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 by dissolution–precipitation processes. (Fig. 2, ESI,† S5, Fig. S5.1 and S5.2).

The simple concept of synthesising NPs by using Nafion's cavities ends up being a very complex scenario that can give rise to uncommonly 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

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, Membrane Science and Technology, Elsevier, 2004, series 9, p. 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., 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. Mol. Catal. A: Chem., 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. Atorngitjawat, 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. Viguès, J. Mas, M. Muñoz, D. N. Muraviev and J. Macanás, Solvent Extr. Ion Exch., 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. Kweskin, 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 and 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, J. Cryst. Growth, 1988, 90, 14.