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# Porous silicon preparation by electrochemical etching in ionic liquids

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2  
3 **Keywords:** porous silicon, electrochemical etching, HF-free, fluorescence, confocal  
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7 microscopy, green chemistry.  
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15 **Abstract:** Anodic etching of n-type {111} silicon in ionic liquid (IL) systems ([RMIM][X], R  
16 = H, Bu; X = BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>), realized under galvanostatic conditions and room temperature,  
17  
18 allowed the formation of porous silicon surfaces with different pore morphology  
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20 depending on the etching time, current density and the IL used. The study of the effect  
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22 of water content in IL on the etching process has shown water content of 1% to be  
23  
24 optimal. The role of the anion on the etching process was elucidated using 1-  
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26 methylimidazolium tetrafluoroborate ([HMIM][BF<sub>4</sub>]) and 1-methylimidazolium  
27  
28 hexafluorophosphate ([HMIM][PF<sub>6</sub>]) IL systems. [HMIM][BF<sub>4</sub>] was found to be most  
29  
30 efficient for the formation of silicon nanostructured array with a pore size of 30-80 nm.  
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33 The thus prepared porous silicon samples show fluorescence in blue light (475 nm).  
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The NMR spectra of [HMIM][BF<sub>4</sub>] ionic liquid before and after etching does not show

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3 noticeable changes, which makes possible to consider this IL as a potentially recyclable  
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7 etching agent.  
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## 16 Introduction

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21 Silicon-based materials, in particular porous silicon (PSi), are of high demand in the  
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23 materials science. Besides dominating solar cells market<sup>[1-4]</sup> silicon and its porous form  
24  
25 are widely used in various research fields such as optoelectronics,<sup>[5-6]</sup> biosensing<sup>[7-9]</sup> and  
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28 biomedical applications.<sup>[10-16]</sup>  
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36 The primary method of obtaining PSi is oxidative etching of a non-porous silicon  
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38 precursor in hydrofluoric acid solutions.<sup>[17]</sup> In electrochemical version of silicon etching  
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40 in fluoride solutions the process can be carried out both in potentiostatic and in  
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43 galvanostatic mode; the latter option is often preferable because of easier control of the  
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49 process.<sup>[9]</sup>  
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4 Although the extreme safety hazards of hydrofluoric acid for nature and humans are  
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7 well known,<sup>[18]</sup> using HF in PSi production seems unavoidable since it is needed for  
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10 removal of native oxides on silicon surface and for binding silicon in etching products.  
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14 The search for different approaches for replacing HF acid by more environmental-  
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16  
17 friendly agents is of great interest in the field of silicon etching<sup>[19,20]</sup> and in other areas of  
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20 materials science.<sup>[21-23]</sup>  
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25 A method of silicon etching replacing HF with silicophilic reagents, in particular, salts of  
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28 pyridine or N-aromatic bases with tetrafluoroboric acid in an organic solvent was  
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30  
31 previously proposed.<sup>[19]</sup> It should be noted that for etching silicon in such systems, it is  
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33  
34 necessary to use the salts solutions of high concentration. In this regard, etching  
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37 systems based on protic ionic liquids,<sup>[24]</sup> combining solvent and supporting salt in one  
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40 compound<sup>[25-26]</sup> that were successfully used in surface electro-chemistry<sup>[27]</sup> might be  
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43 more promising.  
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Besides entirely merited attention and wide use in almost all chemistry-related areas,<sup>[28-</sup>

<sup>31]</sup> ionic liquids permit to address and in many cases to improve very important ecological issues.

In this work, we propose a simple, environment-friendly, and efficient technique for preparing porous silicon by means of an HF-free electrochemical etching in the ionic liquid medium (primarily derivatives of 1-methylimidazolium, [HMIM][BF<sub>4</sub>]). This method allows one to prepare a uniformly porous silicon surface with the possibility of controlling the pore size.

## Results and discussion

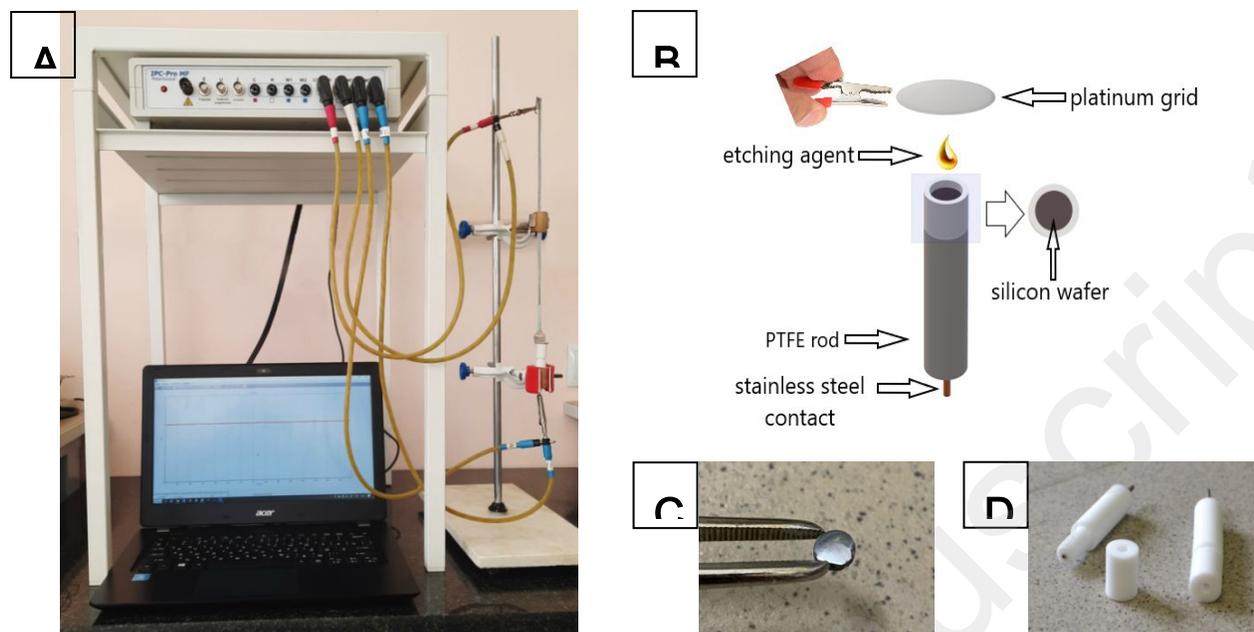
The [HMIM][BF<sub>4</sub>] ionic liquid was synthesized by stirring 1-methylimidazole with tetrafluoroboric acid in appr. 1:1 molar ratio with minimal excess of 1-methylimidazole to prevent the presence of HBF<sub>4</sub> in product. After that, the resulting solution was evaporated, washed with ethyl acetate and dried under vacuum according to <sup>[32]</sup>.

Several samples of [HMIM][BF<sub>4</sub>] were then prepared with a water content of 1%, 5%, and 10%, controlled by Fischer titration.<sup>[33]</sup> Synthesized in the similar way [HMIM][PF<sub>6</sub>]

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4 was conditioned to water content of 2%. In contrast to dry ILs, such wet ionic liquids (w-  
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7 IL) remain liquid at room temperature; this enables using them for silicon etching under  
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10 the ambient conditions without heating which is otherwise needed to liquefy these ILs.  
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15 These w-IL were then tested for etching silicon and revealing the influence of current  
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18 density and etching time on the morphology of the obtained samples.  
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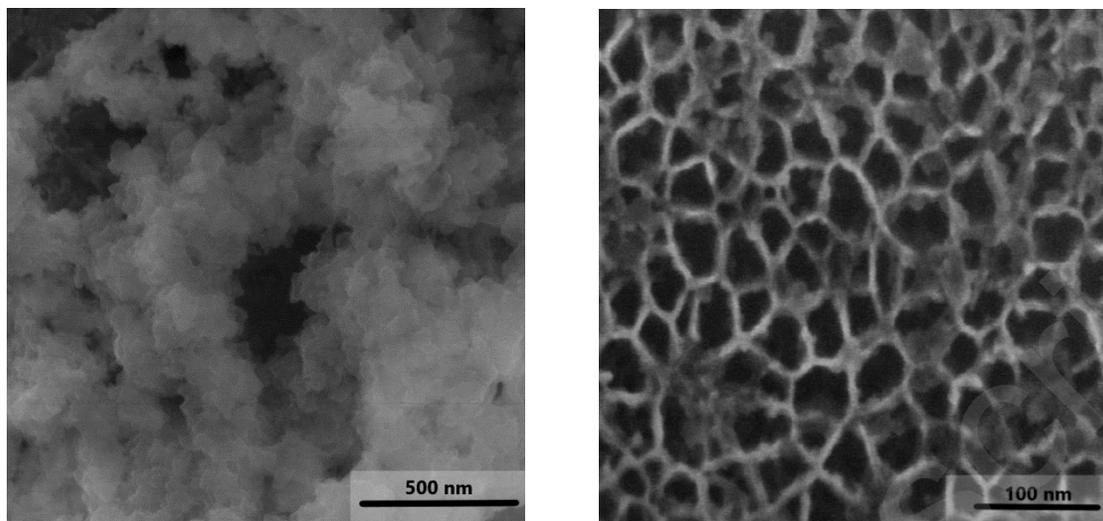
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23 A polished n-type (111) oriented single-crystal silicon wafer was used (Fig. S1) for this  
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26 purpose. The etching was carried out at room temperature in a galvanostatic mode,  
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29 using a specially designed polytetrafluorethylene (PTFE) cell (Fig. 1). The cell was fitted  
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32 with a PTFE nut with a 4 mm hole protecting the Si sample so that the etching area,  
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35 limited by the hole, remains constant throughout all experiments. A platinum grid was  
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38 used as a cathode.  
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**Figure 1.** Photograph of a silicon etching setup (A), the scheme of assembling the etching PTFE cell (B), a polished silicon wafer used in the experiments (C), and a PTFE cell (D) for mounting the sample for etching.

We found that etching in 1% [HMIM][BF<sub>4</sub>] w-IL system at a current density  $j = 8 \text{ mA/cm}^2$  during 30 min results in the development of significant roughness of the surface of silicon wafer (Fig. 2 left). Further increase in etching time leads to the formation of a porous surface.

In particular, a uniform mesoporous surface with the irregularly shaped pores sized of  $31 \pm 2 \text{ nm}$  separated by  $8 \pm 1 \text{ nm}$  walls was obtained after a 5 hours etching (Fig. 2 right).

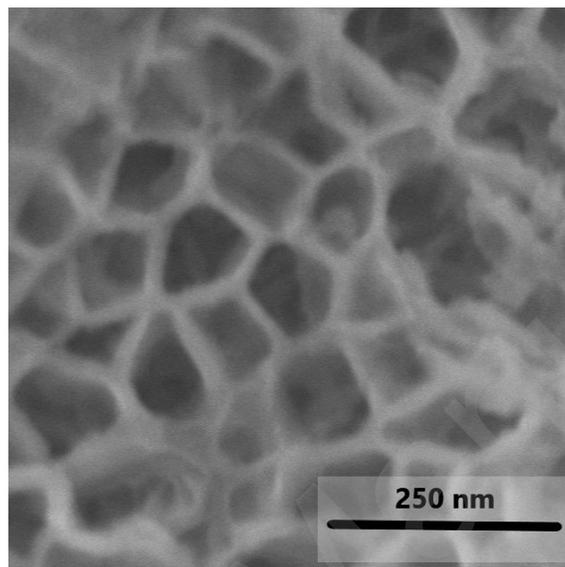


**Figure 2.** Scanning electron microscope (SEM) images of porous silicon obtained by etching in 1% [HMIM][BF<sub>4</sub>] w-IL system at a current density 8 mA/cm<sup>2</sup> during 30 minutes (left) and 5 hours (right).

When etching in HF-based systems, higher current densities are known to increase the pore size and depth.<sup>[34-35]</sup> This trend was also observed during the etching of silicon in [HMIM][BF<sub>4</sub>]-based w-IL system. Fig. 3 shows an scanning electron microscope (SEM) picture of the sample obtained by etching a silicon wafer at  $j = 24 \text{ mA/cm}^2$  for 1 hour.

It can be seen that the pores at thus prepared homogeneous porous surface are larger than those observed after etching for 5 hours at  $j = 8 \text{ mA/cm}^2$ . Now, the pore size and

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3 the thickness of the separating walls are increased up to  $79\pm 6$  nm and  $21\pm 1$  nm,  
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7 respectively. It is noteworthy that the majority of the cells formed are 4 or 5-faceted.  
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32 **Figure 3.** SEM image of porous silicon obtained by etching in 1% [HMIM][BF<sub>4</sub>] w-IL  
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35 system within 1 hour at a current density of 24 mA/cm<sup>2</sup>.  
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40 During etching gas formation is observed, but the change in the amount of water cannot  
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43 be determined within the measurement accuracy, and after the process the system  
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46 remains liquid. It contain white amorphous solid.  
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51 The increase of water content in the IL significantly affects the nature of etching. So, at  
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55 5% water in IL the morphology of the formed layer changed now resembling to a  
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3 network of bulges around deeper etching zones of commensurate size (Fig. S2). This  
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7 case is intermediate between the cellular structure (Fig. 2, 3) and a spongy surface  
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10 when etching is achieved with higher water content (10%) (Fig. S3).  
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15 Elucidating the role of anion in the etching process encounters the intrinsic difficulties of  
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18 strongly varying electrochemical properties of ILs when changing the anion.  
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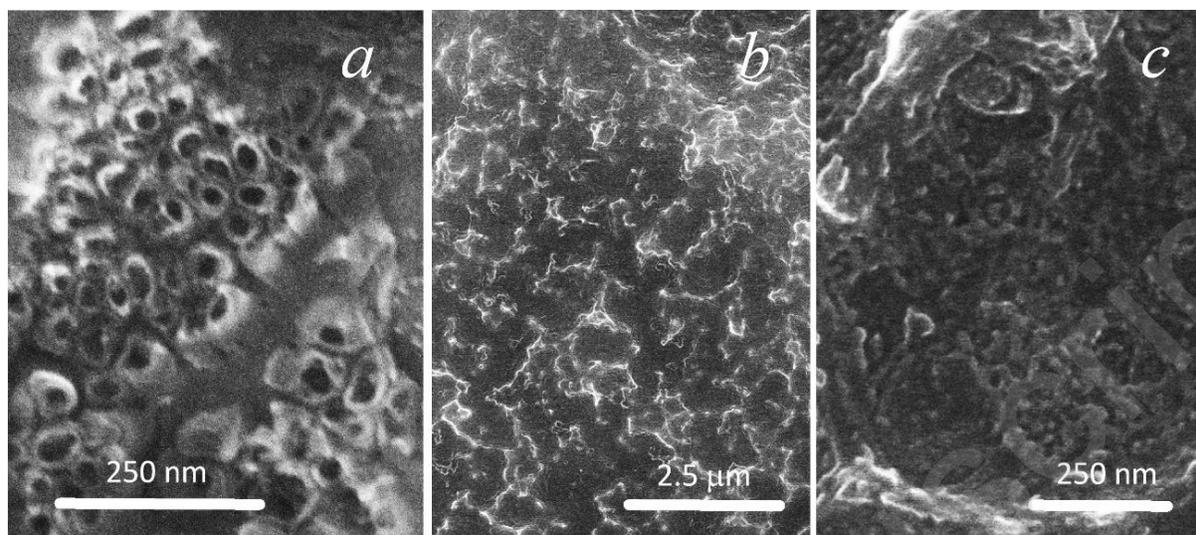
21  
22 Alkylimidazolium ILs with  $\text{PF}_6^-$  anion have about ten times higher viscosity and ten-fold  
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25 lower conductivity than with  $\text{BF}_4^-$ ,<sup>[36]</sup> which dramatically alters etching efficiency with  
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29 [HMIM][ $\text{PF}_6$ ]. The process becomes non-uniform developing locally (Fig. S5, S6),  
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32 though at the bottom of the affected zones the dilution of the IL with etching products  
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35 makes the conditions closer to those with less viscous [HMIM][ $\text{BF}_4$ ] and leads to the  
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38 formation of a similar cellular structure (Fig. S6). Thus, changing the counterion to  $\text{PF}_6^-$   
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42 has significant impact on the surface structure and the viscosity effects point at a  
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45 diffusion-based process.  
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51 When the difference in viscosity/conductivity is smaller, ca. 2 times, finer tuning of  
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54 etching properties is seen. An isotropic electropolishing occurs (Fig. S4) with  
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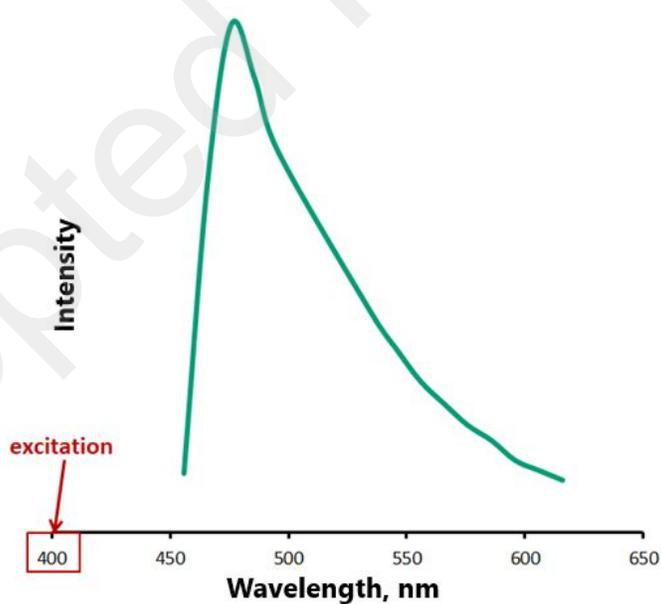
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4 [BMIM][BF<sub>4</sub>] (108.25 cP<sup>[37]</sup> and 3.53 mS/cm<sup>[38]</sup>), whereas an intermediate regime was  
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7 observed with [BMIM][PF<sub>6</sub>] (284.49 cP<sup>[37]</sup> and 1.65 mS/cm<sup>[39]</sup>) when mesoporous  
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10 etching (Fig. 4 a) goes concomitantly with the formation of a sub 100 nm pattern (Fig. 4  
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14 c).

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18 It should be noted that the formation of pores occurs without significant oxidation of the  
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21 silicon surface, as the fraction of silicon oxide in the resulting material is less than 1.5%  
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25 (according energy dispersive X-ray spectroscopy (EDS) data).  
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30 One of the essential qualities of porous silicon is its strong fluorescence.<sup>[40-41]</sup> The  
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33 fluorescence spectrum of a porous silicon sample obtained by etching in 1%  
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36 [HMIM][BF<sub>4</sub>] w-IL system at a current density of 8 mA/cm<sup>2</sup> for 6 hours (Fig. 5) has a  
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40 maximum in blue light at 475 nm. A more detailed study of the optical properties of the  
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44 material is the subject of further study.  
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**Figure 4.** SEM images of a silicon samples etched in w-ILs with  $[PF_6^-]$  anion: (a)  $[HMIM][PF_6]$  (water content 2%) for 1 hour at  $j = 24 \text{ mA/cm}^2$ , (b) and (c)  $[BMIM][PF_6]$  (water content 1%) for 1 hour at  $j = 24 \text{ mA/cm}^2$ .



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4 **Figure 5.** The fluorescence spectrum (excitation at 401 nm) of a porous silicon sample  
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7 obtained by etching in 1% [HMIM][BF<sub>4</sub>] w-IL system during 6 hours at  $j = 8 \text{ mA/cm}^2$ .  
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11 Raman spectra of the studied samples (Fig. S19, S20) are quite similar, with the more  
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13 pronounced 2TO mode of the etched silicon, especially with the 532 nm excitation.  
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19 The IL used for preparing the wafer as in Fig. 2 (right) was diluted with CD<sub>3</sub>CN, and a  
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21 comprehensive range of <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B, and <sup>19</sup>F NMR spectra were recorded. Comparison  
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23 of NMR spectra of this IL before and after etching showed that it does not decompose  
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25 during the etching process (all signals at all nuclei before and after etching are  
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27 completely identical and only the acidic proton signal shifts to the region of the high  
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29 fields, which indicates a some decrease in pH <sup>[42]</sup>) and it can be considered as a  
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31 potentially recyclable etching agent (see Fig. S7-S14). Of course, the interpretation that  
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33 the ionic liquids will be recyclable because there is no degradation of the IL as  
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35 determined by NMR spectroscopy is just a preliminary investigation; and, we will need  
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37 to be examined more closely in the future including examination of the purity of the IL  
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60 after several uses and using a more sensitive technique.

## Experimental

*Reagents, solvents, and materials.* [BMIM][BF<sub>4</sub>] (99 %), used for etching, was supplied by Sigma Aldrich. [BMIM][PF<sub>6</sub>] (99%) was supplied by ABCR. [HMIM][BF<sub>4</sub>] and [HMIM][PF<sub>6</sub>] were prepared from 1-methylimidazol, 99 % (Acros) and fluoroboric acid, 48 wt % (Acros) or hexafluorophosphoric acid, 55 wt % (Sigma Aldrich) respectively.

Ionic liquid systems were washed with ethyl acetate (Acros).

The n-type (111) single-crystalline silicon wafer (d = 5 mm, thickness = 2 mm) was polished to a high gloss with chromium oxide GOI polishing paste and then degreased with isopropyl alcohol (SEM/EDS - see Fig.S1).

*Synthesis of ionic liquids.* [HMIM][BF<sub>4</sub>] was synthesized according to known literary technic.<sup>[32]</sup> The synthesis of [HMIM][PF<sub>6</sub>] was carried out similarly.

The purity and structure of prepared [HMIM][BF<sub>4</sub>], [HMIM][PF<sub>6</sub>] were confirmed by <sup>1</sup>H, <sup>13</sup>C, <sup>11</sup>B, <sup>19</sup>F and <sup>31</sup>P NMR analysis (see SI). The NMR spectra of [HMIM][BF<sub>4</sub>] in CD<sub>3</sub>CN: <sup>1</sup>H NMR (600 MHz): 3.84 (s, 3H, CH<sub>3</sub>), 7.30 (s, H), 7.32 (s, H), 8.26 (s, H),

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3 12.05 (s, N<sup>+</sup>-H). <sup>13</sup>C NMR (150 MHz): 34.2, 116.9, 121.9, 136.8. <sup>11</sup>B NMR (193 MHz): -  
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7 1.06 (s). <sup>19</sup>F NMR (565 MHz): - 150.99 (s, <sup>10</sup>BF<sub>4</sub>) and -151.04 (s, <sup>11</sup>BF<sub>4</sub>) in 1:4 intensity  
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10 ratio, which corresponding to the natural abundance of <sup>10</sup>B and <sup>11</sup>B isotopes in ca. 20%  
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13 and ca. 80%, respectively. The NMR spectra of [HMIM][PF<sub>6</sub>] in D<sub>2</sub>O: <sup>1</sup>H NMR (600  
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15  
16 MHz): 3.65 (s, 3H, CH<sub>3</sub>), 7.16 (s, 2H), 8.37 (s, H). <sup>13</sup>C NMR (150 MHz): 35.3, 119.3,  
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19 122.8, 134.8. <sup>31</sup>P NMR (243 MHz): -145.3 (sep, J = 709.17 Hz) <sup>19</sup>F NMR (565 MHz): -  
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24 72.85 (d, J = 709.14 Hz)  
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29 *NMR spectra* were recorded on Bruker AV600 spectrometer at ambient temperature.

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32 Standards according to Bruker almanac <sup>[43]</sup> were used. Water content in the ILs was  
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35 controlled by Fischer titration using a KAS-01 MD apparatus.  
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40 *Electrochemical etching.* The etching was carried out in a PTFE cell of the original  
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43 design (see Fig. 1). It consisted of a PTFE rod fitted with a PTFE nut with a 4 mm hole  
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46 that allowed the silicon wafer to be pressed against a stainless steel rod, which served  
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49 as a current collector. A PTFE nut also allows us to limit the etching area, so it remains  
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52 constant throughout all experiments. In parallel with the silicon wafer, a platinum grid  
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3 cathode was fixed above the PTFE cell. The etching agent was placed on the surface of  
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7 the silicon wafer using a micropipette. The etching process was carried out in  
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10 galvanostatic mode at current density in the range from 8 mA/cm<sup>2</sup> to 24 mA/cm<sup>2</sup> using a  
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13 PC-piloted digital potentiostat IPC-Pro-MF (Econix). Etching time was varied from 30  
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17 minutes to 6 hours. After that, the silicon wafer was washed with ethyl alcohol and  
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21 stored in a high-purity argon atmosphere in a septum-sealed vial.  
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25 *SEM/EDS*. Morphology of pristine and etched silicon surface was studied using a  
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28 Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). The images  
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32 were acquired in secondary electron mode at 20 kV accelerating voltage and the  
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36 working distance 8-10 mm. Energy-dispersive X-ray spectroscopy (EDS) was carried  
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40 out using an Oxford Instruments X-max 80 EDS system at 20 kV accelerating voltage  
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43 and a working distance 15 mm. The samples were studied without metallization in order  
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46 to avoid metal coating effects.<sup>[44]</sup>  
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4 *Raman spectroscopy.* Raman spectra were acquired with a BWS415 spectrometer  
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7 (BWTEK, Germany) with 785 nm laser, and with EnSpectr532 spectrometer (Enspectr,  
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10 Russia), integrated with 532 nm laser and CX41 microscope (Olympus, Japan).  
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15 *Confocal microscopy.* Confocal microscopy was performed with Nikon A1 confocal  
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18 microscope equipped with 401 nm and 514 nm lasers and spectral detector (Nikon,  
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22 Japan).  
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## 26 **Summary**

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31 High-purity porous silicon with uniform and size-controlled pores was produced using  
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34 wet 1-methylimidazolium tetrafluoroborate as the etching solution. Such a non-volatile,  
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37 non-flammable, and chemically and electrochemically stable system is a good  
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41 alternative to commonly used aggressive, toxic and dangerous HF.<sup>[45]</sup>1-  
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45 Methylimidazolium tetrafluoroborate is easily synthesized and does not require special  
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48 storage conditions. Moreover, it can be considered as a potentially recyclable etching  
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51 agent. Besides, the etching process is very simple, secure and efficient with no need of  
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55 additional heating, control of potential or any other special precautions. All this makes  
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3 the proposed technique suitable for scaling-up. Application of HF-free solvent-in-salt  
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7 system for eco-friendly etching is a novel approach with excellent practical  
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10 opportunities.  
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### 19 **Conflicts of interest**

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24 There are no conflicts to declare.  
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### 28 **ASSOCIATED CONTENT**

#### 29 30 31 **Supporting Information.**

32  
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37 Additional SEM data, NMR and Raman spectra are provided in the Supporting  
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40  
41 Information.  
42  
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44 This file is available free of charge.  
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### 48 49 **AUTHOR INFORMATION**

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## 21 **Author Contributions**

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4 ABBREVIATIONS

5  
6 [BMIM][BF<sub>4</sub>], 1-Butyl-3-methylimidazolium tetrafluoroborate; EDS, energy dispersive X-  
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9 ray spectroscopy; EMIMF·2.3HF, 1-ethyl-3-methylimidazolium oligofluorohydrogenate;  
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12 IL, ionic liquid; [HMIM][BF<sub>4</sub>], 1-Methylimidazolium tetrafluoroborate; [HMIM][PF<sub>6</sub>], 1-  
13  
14 Methylimidazolium hexafluorophosphate; NMR, nuclear magnetic-resonance; PTFE,  
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17 polytetrafluorethylene; PSi, porous silicon; SEM, scanning electron microscope; w-IL,  
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23 wet ionic liquids.  
24  
25

26  
27  
28 REFERENCES

- 29  
30  
31 1. Shin, D. H.; Kim, J. M.; Jang, C. W.; Kim, J. H.; Kim, S.; Choi, S. H. Effect of  
32  
33  
34 Layer Number and Metal-Chloride Dopant on Multiple Layers of  
35  
36  
37 Graphene/Porous Si Solar Cells. *J. Appl. Phys.* **2018**, 123 (12), 123101.  
38  
39  
40  
41 <https://doi.org/10.1063/1.5013169>.  
42  
43  
44  
45  
46 2. Mohammed, M. S.; Shlaga, R. A. Reflectivity Effect of the PS on Solar Cell  
47  
48  
49 Efficiency. *In Journal of Physics: Conference Series*; **2018**.  
50  
51  
52  
53 <https://doi.org/10.1088/1742-6596/1032/1/012027>.  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 3. Praveenkumar, S.; Lingaraja, D.; Mahiz Mathi, P.; Dinesh Ram, G. An  
5  
6  
7 Experimental Study of Optoelectronic Properties of Porous Silicon for Solar Cell  
8  
9  
10 Application. *Optik (Stuttg)*. **2019**, 178, 216-223.  
11  
12  
13 <https://doi.org/10.1016/j.ijleo.2018.09.176>.  
14  
15  
16  
17  
18 4. Juzeliū Nas, E.; Fray, D. J. Silicon Electrochemistry in Molten Salts. *Chem. Rev.*  
19  
20  
21 **2020**, 120, 3, 1690-1709. <https://doi.org/10.1021/acs.chemrev.9b00428>.  
22  
23  
24  
25  
26 5. Korotcenkov G., Rusu E., How to Improve the Performance of Porous  
27  
28  
29 Silicon-Based Gas and Vapor Sensors? Approaches and Achievements. *Phys.*  
30  
31  
32  
33 *Status Solidi Appl. Mater. Sci.*, **2019**, 216, 1900348.  
34  
35  
36  
37 <https://doi.org/10.1002/pssa.201900348>.  
38  
39  
40  
41 6. Wang J., Jia Z., Metal Nanoparticles/Porous Silicon Microcavity Enhanced  
42  
43  
44  
45 Surface Plasmon Resonance Fluorescence for the Detection of DNA. *Sensors*,  
46  
47  
48 **2018**, 18, 661. <https://doi.org/10.3390/s18020661>.  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 7. Terracciano, M.; Rea, I.; Borbone, N.; Moretta, R.; Oliviero, G.; Piccialli, G.; De  
5  
6  
7 Stefano, L. Porous Silicon-Based Aptasensors: The Next Generation of Label-  
8  
9  
10 Free Devices for Health Monitoring. *Molecules* **2019**, 24 (12), 2216.  
11  
12  
13  
14 <https://doi.org/10.3390/molecules24122216>.  
15  
16  
17  
18 8. Ge, D.; Shi, J.; Wei, J.; Zhang, L.; Zhang, Z. Optical Sensing Analysis of Bilayer  
19  
20  
21 Porous Silicon Nanostructure. *J. Phys. Chem. Solids* **2019**, 130, 217–221.  
22  
23  
24  
25 <https://doi.org/10.1016/j.jpcs.2019.03.002>.  
26  
27  
28  
29 9. Harraz, F. A. Porous Silicon Chemical Sensors and Biosensors: A Review.  
30  
31  
32  
33 *Sensors Actuators, B Chem.* **2014**, 202, 897-912.  
34  
35  
36  
37 <https://doi.org/10.1016/j.snb.2014.06.048>.  
38  
39  
40  
41 10. Gopal, S.; Chiappini, C.; Penders, J.; Leonardo, V.; Seong, H.; Rothery, S.;  
42  
43  
44 Korchev, Y.; Shevchuk, A.; Stevens, M. M. Porous Silicon Nanoneedles  
45  
46  
47 Modulate Endocytosis to Deliver Biological Payloads. *Adv. Mater.* **2019**, 31  
48  
49  
50  
51 (12), 1806788. <https://doi.org/10.1002/adma.201806788>.  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 11. Park, Y.; Yoo, J.; Kang, M. H.; Kwon, W.; Joo, J. Photoluminescent and  
5  
6  
7 Biodegradable Porous Silicon Nanoparticles for Biomedical Imaging. *J. Mater.*  
8  
9  
10 *Chem. B.* **2019**, *7*, 6271-6292. <https://doi.org/10.1039/c9tb01042d>.  
11  
12  
13  
14  
15 12. Santos, H. A.; Mäkilä, E.; Airaksinen, A. J.; Bimbo, L. M.; Hirvonen, J. Porous  
16  
17  
18 Silicon Nanoparticles for Nanomedicine: Preparation and Biomedical  
19  
20  
21  
22 Applications. *Nanomedicine.* **2014**, *9*, 535–554.  
23  
24  
25 <https://doi.org/10.2217/nnm.13.223>.  
26  
27  
28  
29  
30 13. Tieu, T.; Alba, M.; Elnathan, R.; Cifuentes-Rius, A.; Voelcker, N. H. Advances in  
31  
32  
33 Porous Silicon-Based Nanomaterials for Diagnostic and Therapeutic  
34  
35  
36  
37 Applications. *Adv. Ther.* **2019**, *2* (1), 1800095.  
38  
39  
40 <https://doi.org/10.1002/adtp.201800095>.  
41  
42  
43  
44  
45 14. Zhang, D. X.; Esser, L.; Vasani, R. B.; Thissen, H.; Voelcker, N. H. Porous  
46  
47  
48 Silicon Nanomaterials: Recent Advances in Surface Engineering for Controlled  
49  
50  
51  
52 Drug-Delivery Applications. *Nanomedicine.* **2019**, *14*, 3213–3230.  
53  
54  
55 <https://doi.org/10.2217/nnm-2019-0167>.  
56  
57  
58  
59  
60

- 1  
2  
3  
4 15. Alhmoud, H., Brodoceanu, D., Elnathan, R., Kraus, T., Voelcker, N.H., A  
5  
6  
7 MACEing Silicon: Towards single-step etching of defined porous  
8  
9  
10 nanostructures for biomedicine, *Progress in Materials Science*. **2019**, 100636.  
11  
12  
13  
14 doi: <https://doi.org/10.1016/j.pmatsci.2019.100636>.  
15  
16  
17  
18 16. Jones, E. C. L.; Bimbo, L. M. Crystallisation Behaviour of Pharmaceutical  
19  
20  
21 Compounds Confined within Mesoporous Silicon. *Pharmaceutics* **2020**, 12 (3),  
22  
23  
24 214. <https://doi.org/10.3390/pharmaceutics12030214>.  
25  
26  
27  
28  
29 17. E. Quiroga-González, H. Föll, In: Porous Silicon: From Formation to Application,  
30  
31  
32 Ed. G. Korotchenkov, Ch.2, CRC Press, 2016, 29-46.  
33  
34  
35  
36  
37 18. Peng, J.; Liu, R.; Peng, L.; Jia, H. Calcium Gluconate Alleviates the Toxic Effect  
38  
39  
40 of Hydrofluoric Acid on Human Dermal Fibroblasts through the Wnt/B-catenin  
41  
42  
43  
44 Pathway. *Oncol. Lett.* **2018**, 16 (3), 2921–2928.  
45  
46  
47  
48 <https://doi.org/10.3892/ol.2018.8975>.  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 19. V. Jouikov, A. Zizumbo, Eur. Pat. 16305617.9, 27.05.2016.  
5  
6  
7 <https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2017203063>,  
8  
9  
10 accessed 10.06.2020.  
11  
12  
13  
14  
15 20. Zhao, S.; Zhang, Q.; Lv, Y.; Wang, X. An HF-Free Etching of SiO<sub>2</sub> for Soft  
16  
17  
18 Lithography. *IEEE Trans. Nanotechnol.* **2016**, 15 (4), 666–670.  
19  
20  
21 <https://doi.org/10.1109/TNANO.2016.2572120>.  
22  
23  
24  
25  
26 21. Kumar, V.; Potdevin, A.; Boutinaud, P.; Boyer, D. HF-Free Synthesis of K<sub>2</sub>SiF<sub>6</sub>  
27  
28  
29 and BaSiF<sub>6</sub> Nanoparticles by Thermal Decomposition. *Mater. Lett.* **2020**, 261,  
30  
31  
32 127123. <https://doi.org/10.1016/j.matlet.2019.127123>.  
33  
34  
35  
36  
37  
38 22. Teo, W. L.; Ariff, S. K. B.; Zhou, W.; Jana, D.; Phua, S. Z. F.; Zhao, Y. Solvent-  
39  
40  
41 and HF-Free Synthesis of Flexible Chromium-Based MIL-53 and MIL-88B.  
42  
43  
44 *ChemNanoMat* **2020**, 6 (2), 204–207. <https://doi.org/10.1002/cnma.201900665>.  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 23. Fialho, L.; Almeida Alves, C. F.; Marques, L. S.; Carvalho, S. Development of  
5  
6  
7 Stacked Porous Tantalum Oxide Layers by Anodization. *Appl. Surf. Sci.* **2020**,  
8  
9  
10 511, 145542. <https://doi.org/10.1016/j.apsusc.2020.145542>.  
11  
12  
13  
14  
15 24. Greaves T. L., Drummond C. J., Protic ionic liquids: properties and applications.  
16  
17  
18 *Chem. Rev.* **2008**, 108, 206-237. <https://doi.org/10.1021/cr068040u>.  
19  
20  
21  
22  
23 25. Buzzeo M.C., Evans R.G., and Compton R.G., Non-haloaluminate room-  
24  
25  
26 temperature ionic liquids in electrochemistry—a review. *ChemPhysChem*, **2004**,  
27  
28  
29 5, 1106-1120. <https://doi.org/10.1002/cphc.200301017>.  
30  
31  
32  
33  
34 26. Silvester D.S., Compton R.G., Electrochemistry in Room Temperature Ionic  
35  
36  
37 Liquids: A Review and Some Possible Applications. *Zeitschrift Für*  
38  
39  
40 *Physikalische Chemie*, **2006**, 220(10), 1247–1274.  
41  
42 <https://doi.org/10.1524/zpch.2006.220.10.1247>.  
43  
44  
45  
46  
47  
48  
49 27. Liu H., Liu Y., Li J., Ionic liquids in surface electrochemistry. *Phys. Chem. Chem.*  
50  
51  
52 *Phys.*, **2010**, 12, 1685-1697. <https://doi.org/10.1039/B921469K>  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 28. Cvjetko Bubalo, M.; Vidović, S.; Radojčić Redovniković, I.; Jokić, S. Green  
5  
6  
7 Solvents for Green Technologies. *J. Chem. Technol. Biotechnol.* **2015**, *90* (9),  
8  
9  
10 1631–1639. <https://doi.org/10.1002/jctb.4668>.  
11  
12  
13  
14  
15 29. Yoo, C. G.; Pu, Y.; Ragauskas, A. J. Ionic Liquids: Promising Green Solvents for  
16  
17  
18 Lignocellulosic Biomass Utilization. *Curr. Opin. Green Sustain. Chem.*, **2017**, *5*,  
19  
20  
21 5–11. <https://doi.org/10.1016/j.cogsc.2017.03.003>.  
22  
23  
24  
25  
26 30. Earle, M. J.; Seddon, K. R. Ionic Liquids. Green Solvents for the Future. *Pure*  
27  
28  
29 *and Applied Chemistry*, **2000**, *72*, 1391.  
30  
31  
32  
33 <https://doi.org/10.1351/pac200072071391>.  
34  
35  
36  
37  
38 31. Egorova, K. S.; Gordeev, E. G.; Ananikov, V. P. Biological Activity of Ionic  
39  
40  
41 Liquids and Their Application in Pharmaceuticals and Medicine. *Chem. Rev.*,  
42  
43  
44 **2017**, *117*, 7132–7189. <https://doi.org/10.1021/acs.chemrev.6b00562>.  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 32. Janus E., Goc-Maciejewska I., Łozyn´ski M., Pernakb J., Diels–Alder reaction in  
5  
6  
7 protic ionic liquids. *Tetrahedron Lett.* **2006**, 47, 4079-4083.  
8  
9  
10 <https://doi.org/10.1016/j.tetlet.2006.03.172>.  
11  
12  
13  
14  
15 33. Azov, V. A.; Egorova, K. S.; Seitkalieva, M. M.; Kashin, A. S.; Ananikov, V. P.  
16  
17  
18 “Solvent-in-Salt” Systems for Design of New Materials in Chemistry, Biology  
19  
20  
21 and Energy Research. *Chem. Soc. Rev.*, **2018**, 47, 1250–1284.  
22  
23  
24 <https://doi.org/10.1039/c7cs00547d>.  
25  
26  
27  
28  
29  
30 34. Ramizy A., Ibrahim I. M., Hammadi M. A., The Effect of Etching Current Density  
31  
32  
33 on Porous Silicon Fabricated by Electrochemical Etching Process. *International*  
34  
35  
36 *Journal of Scientific & Engineering Research*, **2016**, 7 (4) 717-722.  
37  
38  
39  
40  
41 35. Al-Husseini A. M., Influence of Current Density on Morphology of  
42  
43  
44 Electrochemically Formed Porous Silicon. *Jordan J Phys*, **2016**, 9, 47.  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 36. Susan M. A. B. H., Noda A., Mitsushima S., Watanabe M., Brønsted acid–base  
5  
6  
7 ionic liquids and their use as new materials for anhydrous proton conductors.  
8  
9  
10 *Chem. Comm.* **2003**, 938-939. <https://doi.org/10.1039/B300959A>  
11  
12  
13  
14  
15 37. Datasheets, SOLVIONIC SASite SME, [www.solvionic.com](http://www.solvionic.com), accessed  
16  
17  
18 10.06.2020.  
19  
20  
21  
22  
23 38. Stoppa A., Hunger J., Buchner R., Conductivities of Binary Mixtures of Ionic  
24  
25  
26 Liquids with Polar Solvents. *J. Chem. Eng. Data* **2009**, 54, 2, 472-479.  
27  
28  
29 <https://doi.org/10.1021/je800468h>  
30  
31  
32  
33  
34 39. Nakamura K., Shikata T., Systematic Dielectric and NMR Study of the Ionic  
35  
36  
37 Liquid 1-Alkyl-3-Methyl Imidazolium. *ChemPhysChem*, **2010**, 11(1), 285-294.  
38  
39  
40 <https://doi.org/10.1002/cphc.200900642>  
41  
42  
43  
44  
45  
46 40. Gu, L.; Hall, D. J.; Qin, Z.; Anglin, E.; Joo, J.; Mooney, D. J.; Howell, S. B.; Sailor,  
47  
48  
49 M. J. In Vivo Time-Gated Fluorescence Imaging with Biodegradable  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

1  
2  
3 Luminescent Porous Silicon Nanoparticles. *Nat. Commun.* **2013**, 4 (1), 1–7.

4  
5  
6  
7 <https://doi.org/10.1038/ncomms3326>.

8  
9  
10  
11 41. Liu, C.; Jia, Z.; Lv, X.; Lv, C.; Shi, F. Enhancement of QDs' Fluorescence Based  
12 on Porous Silicon Bragg Mirror. *Phys. B Condens. Matter* **2015**, 457, 263–268.

13  
14  
15  
16  
17  
18 <https://doi.org/10.1016/j.physb.2014.10.005>.

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22 42. It should be noted that the technique for producing IL involves addition of acid to  
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27 1-methylimidazole, and in order to exclude the presence of acid in the product  
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30 the latter is taken in a minimal excess. The impurity of 1-methylimidazole in the  
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34 product is removed by repeated extraction with ethyl acetate. The resulting  
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37 product is pure [HMIM][BF<sub>4</sub>] that has a characteristic shift of the acidic proton in  
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40 acetonitrile near 12 ppm, which is identical to the published data (see Ref. 32).

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44 Taking into account the liquid state of the salt, it is actually a non-buffered  
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47 solution with acid-base equilibrium. During etching, 1-methylimidazole, partially  
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51 formed by dissociation of the salt, can be oxidized and an appearing impurity of  
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54 HBF<sub>4</sub>, even in such a small amount not being detected in all spectral data (the  
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3 shifts of all other protons remain the same after etching,  $^{11}\text{B}$  and  $^{19}\text{F}$  spectra  
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7 are also identical), can cause a significant high field shift of the acidic proton. In  
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10 support of this explanation, we have taken a cyclic voltammetry measurement  
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13 of [HMIM][BF<sub>4</sub>] under the same conditions as were during etching but in the  
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16 presence of 1-methylimidazole. It was revealed that its oxidation begins at  
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19 rather low potentials, namely +0.8 V vs. Ag/AgCl (the wave does not have a  
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22 pronounced maximum because of high viscosity of the system), which is  
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25 significantly lower than the real etching potential (> 2 V vs. Ag/AgCl). Also  $^1\text{H}$   
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28 NMR measurement of [HMIM][BF<sub>4</sub>] in acetonitrile showed that the presence of  
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32 3 mol% HBF<sub>4</sub> (a minimal amount that can be added to a NMR tube with  
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35 reasonable accuracy) causes a high field shift of the acidic NH-proton signal by  
36  
37  
38  
39  
40  
41  
42 3 ppm.  
43  
44  
45

46 43. Bruker corporation, Almanac, 2010, ISBN 978-3-929431-24-7, *Chemical Shift*

47  
48  
49 *Ranges and Standards for Selected Nuclei*, <https://www.pascal->

50  
51  
52  
53 [man.com/pulseprogram/Almanac2010.pdf](https://www.pascal-man.com/pulseprogram/Almanac2010.pdf), accessed 10.06.2020  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3  
4 44. Kashin, A. S.; Ananikov, V. P. A SEM Study of Nanosized Metal Films and Metal  
5  
6  
7 Nanoparticles Obtained by Magnetron Sputtering. *Russ. Chem. Bull.* **2011**, 60  
8  
9  
10 (12), 2602–2607. <https://doi.org/10.1007/s11172-011-0399-x>.  
11  
12  
13  
14  
15 45. It should be noted that a technique of etching silicon using ionic liquid 1-ethyl-3-  
16  
17  
18 methylimidazolium oligofluorohydrogenate (EMIMF·2.3HF) has been published  
19  
20  
21 in the literature. However, HF is also actually present in such a system. Raz,  
22  
23  
24 O., Starosvetsky, D., Tsuda, T., Nohira, T., Hagiwara, R., Ein-Eli, Y.  
25  
26  
27  
28  
29 Macroporous Silicon Formation on n-Si in Room-Temperature  
30  
31  
32 Fluorohydrogenate Ionic Liquid, *Electrochem. Solid-State Lett.*, **2007**, 10, D25-  
33  
34  
35  
36 D28. <https://doi.org/10.1149/1.2409058>.  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
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