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Brenda Omaña-Sanz, Djadidi Toybou, Ludovic Lesven, Valérie Gaucher, Alexandre Fadel, et al.. An electrochemical method to rapidly assess the environmental risk of silver release from nanowire transparent conductive films. *NanoImpact*, 2020, 18, pp.100217. 10.1016/j.impact.2020.100217 . hal-02990833

HAL Id: hal-02990833

<https://hal.science/hal-02990833>

Submitted on 18 Nov 2020

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1 An electrochemical method to rapidly assess the
2 environmental risk of silver release from nanowire
3 transparent conductive films

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27 Keywords

28 Silver nanowire networks – polysiloxane coatings – electrochemical corrosion – accelerated
29 aging – silver exposure

30

31 ABSTRACT

32 Silver nanowires (AgNW) are new nanomaterials designed to be incorporated into transparent
33 conductive films in electronics, microelectrodes, heated surfaces and others. Although in
34 these films, the AgNW are generally protected by a coating material, a risk for release of
35 silver at all stages of the nanoproduct life cycle does exist due to corrodibility of the metal.
36 Since ionic and nanoparticulate Ag represent a toxicological risk for a large number of living
37 cells, there is a need for quantifying the potential Ag release from these product components.
38 We developed an electrochemical method to evaluate possible corrosion activity of silver in
39 AgNW transparent conductive films (TCFs) and concomitant Ag⁺ release. A polysiloxane
40 polymer was used as protective coating of AgNW TCFs. A consistent correlation is observed
41 between the degree of corrosion and the coatings' characteristics, in particular the thicknesses.
42 A major advantage of the new approach, compared to classical aging studies, is the short
43 experimentation time: 20 min are sufficient for a diagnostic result. The method is an
44 accelerated corrosion and release test. It is green methodology with use of very low electric
45 power and with no harmful reagents. A particularly attractive application could be in the field
46 of environmental risk assessment of metals from portable electronics and biosensors.

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57 **1. Introduction**

58 Silver nanowires (AgNWs) are one of the most promising alternative engineered
59 nanomaterials (ENMs) to replace indium tin oxide (ITO) in transparent electrodes (Sannicola
60 et al., 2016). Random networks of AgNWs are being used for transparent conductive films
61 (TCFs) to be applied in a wide range of technological applications from optoelectronics to
62 heatable films and biomedical devices (Doganay et al., 2016; He and Ye, 2015; Toybou et al.,
63 2019; Zhang and Engholm, 2018). The interconnection of metallic nanowires, e.g. AgNWs,
64 creates electric conductive paths allowing electrical current flow.

65 It is known that metallic silver is corroded when exposed to atmospheric conditions;
66 similarly silver nanowires are also easily corroded (Graedel, 1992; Molleman and Hiemstra,
67 2017), thereby causing failures in conductive networks. To counter this problem, application
68 of a nano to micrometer thick layer of a protective coating material over the conductive NW
69 network, before its integration into a device, is often performed in order to stop the diffusion
70 of water vapor and gases, thus to avoid corrosion. Other external damages like scratches and
71 bends are also avoided by this protection.

72 Different materials have been considered for creation of a protective coating, including
73 reduced graphene oxide (Ahn et al., 2012; Duan et al., 2019), metal oxides and carbonates
74 (Jeong et al., 2019; Khan et al., 2018), optical adhesive (Miller et al., 2013), chitosan (Jin et
75 al., 2017), and polymers (Chen et al., 2014; Kim et al., 2015; Miao et al., 2019; Moreno et al.,
76 2013; Xu and Zhu, 2012). Although the coatings could delay corrosion, 100 % of
77 effectiveness on the long-term still remains an issue (Deignan and Goldthorpe, 2017; Jiu et
78 al., 2015). A noticeable factor is that most of the protective coating materials in use,
79 especially polymers have some degree of permeability at the molecular level.

80 Besides the permeability aspect, wear and tear of the NW containing products throughout
81 their life cycle, i.e. from their active use to end-of-life disposal, may degrade the mechanical
82 and chemical quality of the conductive film and enhance the corrosion of the nanowires.

83 Corrosion is responsible for the release of ionic silver and the formation of nanoscopic wire
84 debris. These forms of silver are toxic at low levels to aquatic organisms and microorganisms,
85 and to certain types of human cells (Lehmann et al., 2018; Liao et al., 2019). Corrosion of
86 AgNW TCFs may lead to critical silver exposure of the device user and/or to pollution of the
87 receiving environment.

88 According to the inventory of available databases e.g. the Nanodatabase, R-Nano and
89 StatNano (R-Nano.fr, <https://www.r-nano.fr>; STATNANO, <https://statnano.com/>; The
90 Nanodatabase, <http://nanodb.dk/>), the number of household products and biomedical devices
91 incorporating nano-silver is rapidly expanding (Bodycap, [http://www.bodycap-
93 medical.com/fr/](http://www.bodycap-
92 medical.com/fr/); Naidu et al., 2015; Rajsiki et al., 2019; Yao et al., 2017). Despite this fact,
93 there is currently a lack of information on toxicological (Lehmann et al., 2019) and eco-
94 toxicological effects of this widespread occurrence of trace silver. Studies concerning silver
95 release have mainly focused on textiles (Part et al., 2018). Standardized risk assessment
96 methods for nanowires is still missing.

97 Very few predictive models of Ag-ENM fate in the environment have been conducted with
98 data from provenances other than textiles (Giese et al., 2018; Sun et al., 2016). Concerning
99 silver nanowires, previous studies mainly focused on technical quality control of AgNW
100 transparent electrodes, in particular on lifetime stability of the devices (Deignan and
101 Goldthorpe, 2017; Elechiguerra et al., 2005; Jiu et al., 2015; Khaligh and Goldthorpe, 2013;
102 Lin et al., 2018; Mayousse et al., 2015). To our knowledge, this is the first investigation to
103 evaluate the capacity of AgNW in TCFs to corrode (hereafter referred to as corrodibility), in
104 order to assess the risk of metal release to users and the environment. In this work, we
105 developed an electrochemical method where corrosive conditions are imposed on AgNW TCF
106 under aqueous conditions, to evaluate the potential for formation of ionic silver and tiny
107 debris of nanowires and their transport from inside to outside the conducting film. An

108 accelerated corrosion test is developed, completed within 20 min. Moreover, it can be
109 considered green methodology as only very low electric power is needed and no chemical
110 reagents other than tiny amounts of standard electrolyte salt are used.

111 The paper reports corrosion experiments conducted with AgNW films, either uncoated or
112 coated with a protective layer of anti-scratch varnish AE12® of different thicknesses. Some
113 AgNW films underwent natural alteration prior to experiments. These samples were
114 considered as “pre-aged” and representative of nanoproducts during their life cycle or at end
115 of life. Two commercial products were also investigated.

116

117 **2. Materials and Methods**

118 *2.1. AgNW film samples*

119 AgNW networks were deposited on large dimension transparent flexible substrate (10 x 10
120 cm) of polyethylene naphthalate (PEN), called hereafter “AgNW large plate”. These large
121 plates were used to prepare the “AgNW film” samples used in the corrosion experiments. The
122 synthesis of AgNWs was conducted following the polyol method, the preparation of the large
123 plates is described in Mayousse et al. (2013). The initial sheet resistances of AgNW large
124 plates varied from 8 to 26 Ω/\square . The nanowires used had diameters in the range 50-90 nm and
125 lengths between 6-26 μm (SI appendix, Table S1) according to control measurements
126 conducted with ImageJ software on FESEM images.

127 The AgNW large plates, when received, had an age of several months to more than one year
128 and thus showed different degrees of aging. A thorough electron microscopic investigation
129 was conducted on each plate before use, in order to discard damaged specimens not suitable
130 for the experiments, or amenable to misleading interpretations.

131 To prepare the AgNW film samples, the AgNW large plates described above were cut into
132 2.5 x 3.5 cm^2 pieces, hereafter referred to as AgNW TCF or AgNW film. At least 3 samples

133 were prepared from each AgNW large plate in order to assure reproducibility of results. Part
134 of the samples were coated with a polysiloxane polymer (anti-scratch varnish AE12®, from
135 ISOCHEM) used as a non-conductive coating material to protect the AgNW films used in the
136 experiments (see details in SI appendix). Coating thicknesses of 500 and 700 nm (mean
137 values) were achieved by varying the spin coating parameters. Polysiloxane is one of the
138 materials studied as potential candidate for TCF coatings. According the findings by Toybou
139 (2018), this coating effectively preserves the AgNW TCF under ambient degradation
140 conditions and seems to improve initial conduction performances of the samples.

141 In addition, AgNW films of $2.5 \times 3.5 \text{ cm}^2$ size, readily coated (by dip coating) with a
142 protective layer of $5 \mu\text{m}$ thickness (mean value), were prepared from new materials that had
143 not undergone any aging prior to the experiments in this study.

144 Two commercial products were also tested with the method developed here. A silver
145 antibacterial textile (silver-coated fibers) and heatable glasses from a skiing goggle containing
146 silver ENM. Both products were purchased specifically for the experiments. The skiing
147 goggle glasses were composed of a layer containing the ENMs and protected with a very thick
148 over-coating layer of a polymer called polycarbonite by the manufacturer. For the
149 experiments, both materials were cut into pieces of $2.5 \times 3.5 \text{ cm}^2$.

150

151 *2.2. Sample characterization*

152 The effect of the corrosion experiments on the AgNW films were evaluated by Field
153 Emission Scanning Electron Microscopy (FESEM) using a JEOL JSM-7800F LV equipped
154 with EDS/EBSD system, and a FEI Quanta 200 environmental scanning electron microscope
155 (ESEM). The observations by FESEM were performed at 5 kV on coated AgNW films and at
156 15 kV on uncoated AgNW films. The observations by ESEM were conducted at 20 kV. Both
157 secondary electron (SE) and electron backscattering (BSE) modes of imaging were used. To

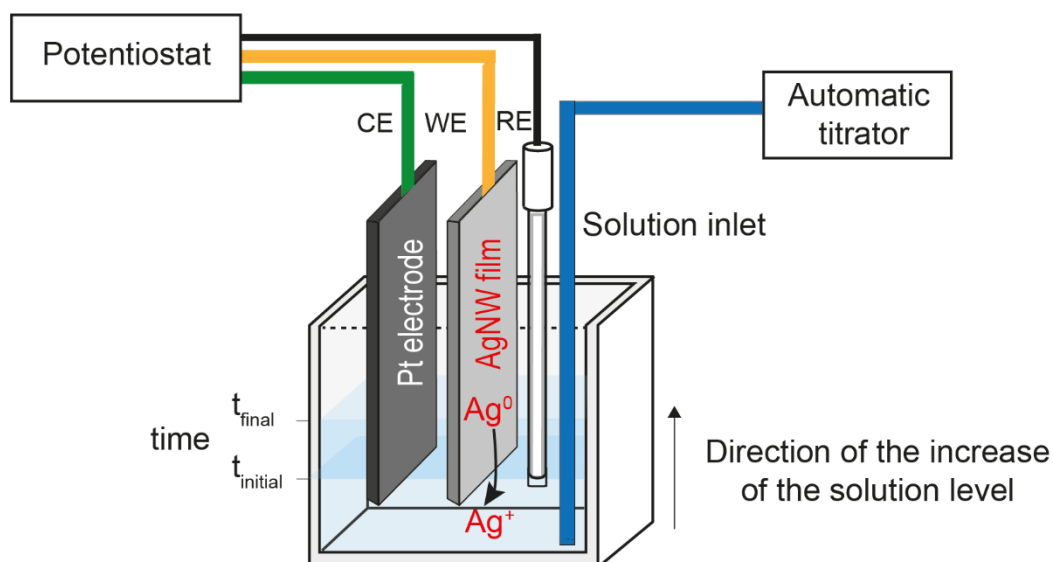
158 avoid surface charging, samples were chromium coated (70 Å) by electro-sputting under
159 vacuum prior to FESEM observations.

160 Atomic force microscopy (AFM) topographic observations and roughness measurements
161 were carried out on a Dimension 3100 apparatus from Digital Instruments operated in
162 Tapping Mode, using a set-point amplitude ratio close to 0.9 in order to reduce indentation
163 effects and thereby optimize the topographic contrast. The Nanoworld silicon SPM sensors
164 had a tip radius less than 10 nm, the nominal spring constant and resonance frequency of the
165 cantilever being around respectively 50 N m^{-1} and 250 kHz.

166 *2.3. Corrosion cell*

167 The corrosion experiments were carried out in an electrochemical cell in a three electrode
168 configuration (Figure 1). The AgNW film of $2.5 \times 3.5 \text{ cm}^2$ was used as the anode, a platinum
169 grid of similar size as the cathode. A mercury/mercurous sulfate electrode was used as
170 reference. The electrochemical cell, specially designed for the experiments, made of PTFE,
171 consists of a rectangular chamber of 10 mL volume, with two facing walls of the size of the
172 electrodes. In the chamber top, slots are foreseen for positioning cathode and anode, and a
173 hole for insertion of the reference electrode. The inter-electrode distance between anode and
174 cathode is 0.5 cm. The reference electrode (RE-2CP, ALS Co.) is located outside the anode-
175 cathode path. The electrolyte is introduced into the chamber through another small hole in the
176 chamber top. An automatic titrator (Titroline 7000, SI Analytics) controls solution addition.

177 All experiments were performed in a Faraday cage. A potentiostat (VSP, Bio-Logic) served
178 to set the cell potential and to record the current generated.



180 **Figure 1.** Schematic of the electrochemical corrosion cell used in the corrosion tests. A three-
 181 electrode configuration was used: the AgNW film was used as anode (working electrode
 182 WE), a platinum grid as cathode (counter electrode CE), a mercury/mercurous sulfate
 183 electrode as reference electrode (RE). The automatic titrator allowed constant addition of
 184 solution over the duration of the experiment ($t_{\text{final}} - t_{\text{initial}} = 20$ min). The arrow shows the
 185 direction of increase of the solution level, thus the progression of the provoked corrosion.

186

187 2.4. Experimental conditions

188 NaNO_3 at 0.01 M was used as electrolyte solution (SI appendix, Figure S1). This
 189 concentration is representative of environmental conditions of continental surface and
 190 subsurface waters (Stumm and Morgan, 1996). The 0.01 M NaNO_3 salt solution established
 191 naturally at a pH of 5.0 ± 0.2 . This pH was retained as the working pH because it was well
 192 within the range where polysiloxane is chemically stable (SI appendix) and because this pH is
 193 representative for environmental conditions.

194 We determined the free corrosion potential (E_{corr}) of a 2 mm silver rod (Advent Research
 195 Materials) and of commercial AgNW (2.23% wt/wt dispersion, Nanogap) dispersed onto a
 196 carbon paste electrode. The corrosion potential of these silver materials was 0.45 V, detailed
 197 results can be found in Lehmann et al. (2019). To study corrosion on the AgNW film
 198 electrodes, we applied an overpotential of 0.8 V vs. SHE. At this voltage, the nanowires were
 199 not subject to any Joule heating problem (Khaligh et al., 2017) neither in the aqueous nor in

200 the aerial part of the electrode. Also the water electrolysis reaction ($E^\circ(\text{pH}5) = 0.925 \text{ V}$) is
201 negligibly small at a potential of 0.8 V, thus not interfering with the Ag redox reaction or the
202 pH of the solution.

203 The NaNO_3 electrolyte solutions and the K_2SO_4 0.6 M reference electrode solution were
204 prepared with ultrapure water and analytical grade reagents.

205

206 *2.5. Experimental procedure*

207 The corrosion experiments were conducted in the electrochemical cell under constant
208 addition of electrolyte solution. This allowed to continuously renewing the solution-air
209 contact line on the film surface. The continuous shifting of this “active zone” allowed
210 maintaining high corrosion conditions throughout the experiment. Some tests were also
211 conducted under fixed electrolyte volume conditions (SI appendix, Figure S2 A-B).

212 An initial volume of around 2 mL of electrolyte solution was placed in the reactor chamber,
213 just enough to allow the solution surface to touch the lower edge of the AgNW film. The
214 electric potential (set to 0.8V vs. SHE) and the automatic titrator were switched on
215 simultaneously, thus insuring constant addition of solution over the duration of the experiment
216 and starting at time t_{initial} (Figure 1). A total volume of 2 mL of electrolyte solution was added
217 at a flow rate of $100 \mu\text{L}\cdot\text{min}^{-1}$ (20 min). This flow rate corresponds to a displacement of the
218 solution/air interface inside the reactor chamber of 0.04 cm/min. Preliminary experiments
219 showed that the chosen rate was enough to ensure a constant shift of the interfacial line
220 between solution and air on the AgNW film. Electron microscopic controls showed that the
221 movement is rapid enough to contain the capillary ascent of solution along the nanowires and
222 along the borders of the film. The solution inside the cell was not stirred but the continuous
223 addition of solution induced some degree of turbulent mixing. The pH of the solution, initially
224 at 5, was controlled before and after the experiment. After 20 min, the experiment was

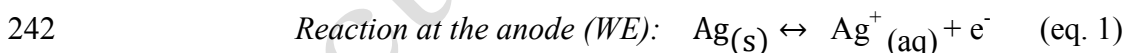
225 stopped, the electrodes were removed carefully and an aliquot of the electrolyte solution was
226 taken for Ag⁺ analysis. The AgNW film sample was removed from the reactor, the area that
227 had been immersed was cut off, carefully rinsed and placed in a desiccator for later surface
228 analysis. The remaining part of the film, which had not been immersed in the electrolyte
229 solution, was used for a subsequent experiment on the same sample.

230 All the solution samples were filtered through 0.2 μm pore size polycarbonate filters (PCTE
231 Sartorius, Fisher Scientific), and several samples were additionally filtered through 10 kDa
232 (equivalent to 4 nm) ultrafiltration membranes (Ultracel, Amicon 25 mm, Merck) using a
233 stirred ultrafiltration cell system (Amicon, model 8010, 10 mL, Merck) in order to separate
234 Ag nanoparticles from the truly dissolved fraction. All filtrates were acidified with HNO₃ 2%
235 trace analysis/ultrapure quality. Analyses of silver concentrations were conducted by
236 Inductively-Coupled Plasma Mass Spectrometry (ICP-MS Agilent 7700x).

237

238 **3. Results and discussion**

239 In the electrochemical cell (Figure 1), the oxidation of silver metal is promoted by using
240 the AgNW TCF as the anode and applying an electric potential higher than the corrosion
241 potential. The silver metal is oxidized and goes into solution in the form of ionic silver (eq. 1).



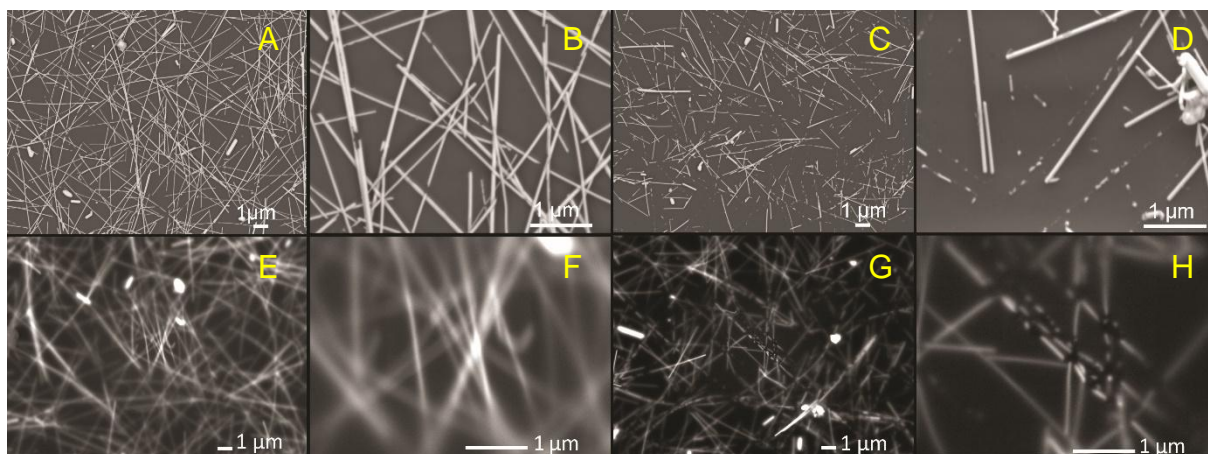
243 In this study, we investigated the corrodibility of polysiloxane coated AgNW films with
244 coating thicknesses varying from thin (500 nm), medium (700 nm) to thick coated (5 μm).
245 Uncoated AgNW films were also studied. Each selected film was submitted to the
246 electrochemical corrosion test. The current response to the applied voltage was recorded via
247 the potentiostat. The raw and qualitative data was then transformed by integrating the traces
248 over the experiment time, to obtain Q the quantity of charge, i.e. a single number
249 representative of a given experiment (calculation details in SI appendix).

250

251 *3.1. Features of corrosion after experiments*

252 As mentioned above, the AgNW large plates available for the preparation of the samples,
253 i.e. the “AgNW films” were carefully studied by Field Emission Scanning Electron
254 Microscopy (FESEM) before use to discard damaged specimens not suitable for the
255 experiments. On the plates kept for the study, the signatures of natural pre-aging processes or
256 of synthesis related defects were identified (SI appendix, Figures S3, S4) so that the effects of
257 our corrosion experiment could be clearly recognized.

258 The characteristic signature of nanowire degradation by electrochemical corrosion (our
259 experiments) appears mainly in the active zone, i.e. along a triple junction line between
260 solution, air and the partly immersed sample. The active zone was continuously renewed by a
261 constant addition of electrolyte solution, thereby maintaining high electrical conduction thus
262 continuous corrosion conditions. Electrochemical corrosion signature was fragmentation of
263 the nanowires into an alignment of nanoparticles and/or nanorods. This feature appeared
264 similarly for uncoated (Figure 2 A-D) and thin-coated AgNW films (Figure 2 E-H).
265 Fragmentation creates discontinuities leading to electrical failure. It has been shown
266 previously that the degradation of an AgNW network is dependent on several network
267 characteristics (Elechiguerra et al., 2005; Mayousse et al., 2015). Our results show that in a
268 given sample, nanowires with smaller diameters were corroded preferentially to thicker
269 nanowires or silver nanoparticle clusters (Figure 2D). When investigating the parameters
270 nanowire diameter and sheet resistance, we observed that small diameters and/or low initial
271 sheet resistances produced higher quantity of charge than large diameters and/or high initial
272 resistances (SI appendix, Figure S5). In other words, corrosion is enhanced in networks with
273 thin nanowires and/or high wire densities (i.e. high initial sheet resistances). Similar trends
274 were described in previous studies (Toybou, 2018).



275

276 **Figure 2.** SEM images (BSE) of AgNW films from plate 5 (NW diameter 57 ± 10 nm, NW
 277 length 7 ± 2 μm) unexposed and exposed to the corrosion test. Each pair of images (e.g. A-B;
 278 C-D, etc) are images of the same film at different magnifications. A-B) Pristine nanowires in
 279 an uncoated film, some silver clusters are seen, an evidence that natural corrosion took place
 280 prior to experiments. C-D) Fragmentation, nanowire discontinuities and formation of
 281 nanoparticles as a result of 20 min of corrosion test. E-F) Pristine nanowires in a film
 282 protected with a thin layer of AE12 coating. G-H) Same film after 20 min of corrosion test;
 283 fragmented nanowires with dissolution gaps appearing dark. Another example of
 284 electrochemical corrosion signatures on AgNW films (from plate 9: NW diameter 86 ± 13 nm
 285 NW length ± 4 μm) can be found in SI appendix, Figure S13.

286

287 In some spots of the AgNW film, roughening of the nanowire surface was observed
 288 together with a decrease in NW brightness. Although this suggested mineral deposition, no
 289 evidence of silver oxide, hydroxide or sulfide on the wire surface was detected by EDS (SI
 290 appendix, Figure S4) maybe due to low amounts of these products particularly in the case of
 291 sulfide, below the detection limits of the technique used (SEM-EDS) as discussed previously
 292 by other authors (Lin et al., 2018; Toybou, 2018). It is most probable that the observed
 293 roughening was due to overgrowths made essentially of elemental silver (Lin et al., 2018). No
 294 sign of melting was observed at NW junctions or at NW tips, discarding the hypothesis of
 295 Joule heating (Khaligh et al., 2017) to contribute to wire failure under our experimental
 296 conditions.

297 In AgNW films with medium coating thickness, similar pattern were observed as described
298 above for thin coated and uncoated films, i.e. highly fragmented networks in the active zone
299 and numerous patches of darkened nanowire surfaces (Figure 2 G-H) (Mayousse et al., 2015).
300 Films coated with a thick layer of polymer ($5 \pm 1\mu\text{m}$) could not be investigated by SEM
301 because of insufficiently electron-transparency of that thick layer.

302 Tiny cubic nanoparticles were observed in some AgNW films (from plates 1 and 9). These
303 nanocubes, precipitates of Ag and Cl, appeared on the surface of nanowires or the surface of
304 the polymer coating in case of coated films. The presence of traces of chlorine in our
305 experimental set-up is attributed to Cl^- impurities contained in AgNW, inherited from the
306 reagents used for NW synthesis and then released upon NW dissolution. Details of this
307 unexpected occurrence of Ag-Cl nanocubes and speciation calculations are discussed in SI
308 appendix, Figures S6-S8.

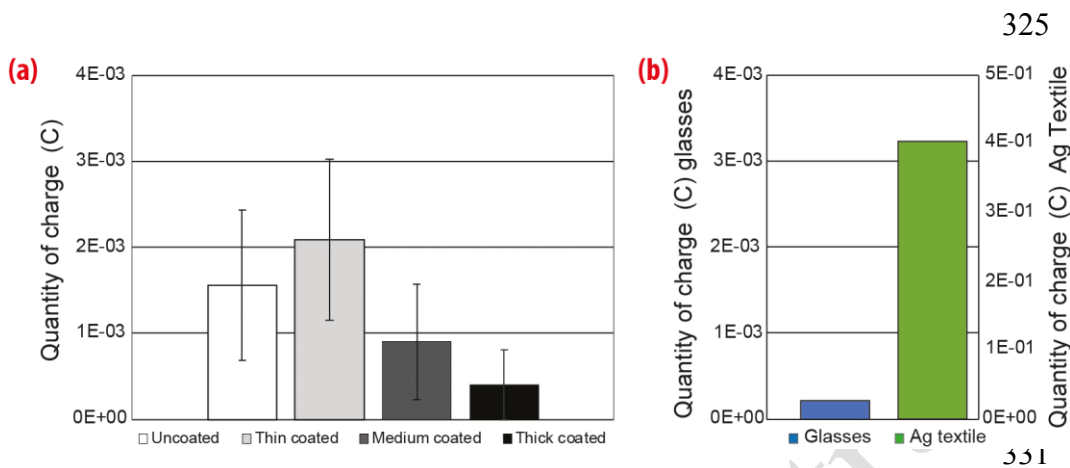
309

310 *3.2. Corrosion of AgNWs as a function of coating layer thickness*

311 The presence of a protective layer on AgNW films and the thickness of this layer play a
312 crucial role in limiting corrosion and failure of AgNW films.

313 Corrosion current responses are presented for four categories of AgNW films (Figure 3.a),
314 from uncoated films to films with a thick coating layer of AE12. Each category includes
315 AgNW films prepared by us (see details in SI appendix Table S1). The results are consistent
316 with expectations, i.e. the developed quantity of charge was higher in experiments with
317 AgNW films with a thin layer of polysiloxane and decreased as the thickness of the protective
318 layer increased (Figure 3.a). For uncoated AgNW films, the quantity of charge developed was
319 lower than for thin coated films, which may reflect loss of NWs during the experiment, due to
320 insufficient adhesion of NWs to the PEN substrate in the unprotected films. It is interesting to
321 highlight that a corrosion current was measured in all cases. Even when the AgNW film was

322 overcoated with a thick layer (5 μm) of protective AE12, an electrical current could still be
 323 measured. Collectively, these results on corrodibility of coated AgNW films indicate that
 324 polysiloxane is permeable to water molecules and Ag^+ ions.



332 **Figure 3.** a) Comparison between quantity of charge (mean values) generated in AgNW films
 333 with varying thicknesses of polysiloxane coating: uncoated, thin (500 nm), medium (700 nm)
 334 and thick (around 5 μm). The high standard deviation values ($n=5$) observed in each bar are
 335 related to the variable qualities of the different plates used (see SI appendix, Figure S12). b)
 336 Quantity of charge for the commercial products tested: heatable glasses containing silver
 337 ENM (blue bar) and silver antibacterial textile (green bar). All the results correspond to
 338 experiments at 0.01 M ionic strength, imposed potential of 0.8 V vs. SHE and pH 5.

339

340 Polymers such as PEDOT:PSS, PVP, PVA, that have often been used as coating materials
 341 (Jiu et al., 2015), are hydrophilic polymers with a plurality of polar groups which tend to sorb
 342 water. Similarly, AE12 polysiloxane used in the present work is also hydrophilic according to
 343 fabricant communication and corroborating results from water contact angle measurements
 344 (SI appendix, Figure S9). Celle et al. (2018) reported a water vapor transmission rate of 80
 345 $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ for a polysiloxane layer of 1.5 μm thickness. The polarity of these polymers
 346 confers them some degree of permeability, which explains why ion diffusion is possible
 347 through the protective layer, therefore why a corrosion current is measured by the
 348 potentiostat.

349 To control that the coating remained intact throughout the experiment, we conducted AFM
 350 surface roughness measurements on the surface of an AgNW thin coated film, on treated and

351 untreated zones. Results (SI appendix, Figure S10) show no significant difference between
352 roughness values in both zones, indicating that the polymeric material exhibits no textural
353 alteration at a scale of tens of nanometers.

354 Electrochemical corrosion results of the two commercial products containing silver, a silver
355 antibacterial textile and a skiing goggle with heatable glasses containing silver ENM (Figure
356 3.b) showed evidence of corrosion in both materials. The skiing goggle glasses (blue bar)
357 generated low corrosion current compared to the quantity of charge measured in the AgNW
358 films of the present study. This result may be related to the very thick layer of protective
359 coating covering the conductive layer. In the case of silver antibacterial textile (green bar), the
360 values were 2 orders of magnitude higher than for the AgNW films.

361 In the next section, the release of ionic silver during the corrosion test will be investigated
362 quantitatively.

364 *3.3. Quantification of dissolved silver (Ag^+)*

365 Silver released from AgNWs during the corrosion experiments was quantified by ICP-MS.
366 To distinguish between nanoparticulate Ag and truly dissolved Ag^+ , the filtration procedure
367 included micro-filtration through a 0.2 μm pore size membrane and ultra-filtration through a
368 10 kDa membrane. Potential sources of silver contamination as well as interactions between
369 Ag^+ and filter materials (i.e. sorption and desorption) were controlled but proved to be non
370 significant under experimental conditions in this study.

371 Silver concentration was measured after each filtration step. Total silver was not quantified
372 systematically due to the limitation of sample volume. Results showed no significant
373 difference in concentration between nanoparticulate-dissolved (0.2 μm) and truly dissolved
374 (10 kDa) fractions (SI appendix, Figure S11). This strongly suggests that the main transfer
375 path of silver from the AgNW film to the solution was via diffusion of Ag^+ through the

376 polymer coating, or via direct diffusion in the case of uncoated AgNW film. In consequence,
377 0.2 μm polycarbonate filtrated solutions were considered as true solutions.

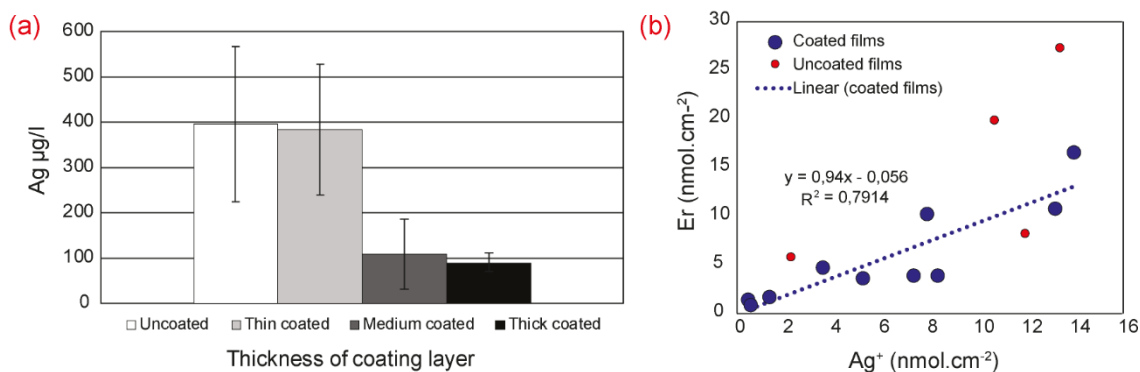
378 In Figure 4.a, concentrations of dissolved silver (originating from AgNW films) are
379 represented as a function of the thickness of the protective coating layer. Clearly, the amount
380 of dissolved silver decreases as the thickness of the protection layer increases. For uncoated
381 films, release of dissolved silver was not significantly higher than for coated films,
382 corroborating the fact that corrosion is limited by detachment of silver nanowires, which
383 thereby modulates the formation of ionic silver. While Figure 4.a shows mean values, single
384 results specific to two given plates are presented in SI appendix, Figure S12.

385 To find out if a direct relation can be established between the amount of Ag^+ detected in
386 solution (by ICP-MS) and the electrochemical results, we converted the parameters quantity
387 of charge, resulting from the corrosion current measured by the potentiostat, and the amount
388 of ionic silver released from AgNW films to comparable units (calculation details in SI
389 appendix).

390 As seen in Figure 4.b, the data sets originating from coated films (blue dots) show a same
391 general trend. A linear correlation can be drawn with a slope of almost 1, suggesting that
392 silver corrosion feeds the electric current with almost no electron loss. Although data are
393 somewhat scattered around the correlation line ($R^2 = 0.79$), this result supports the initial
394 hypothesis that the amount of charge determined for an experiment is representative of the
395 amount of silver released to solution. In contrast, the data sets for uncoated films (red dots)
396 result in very scattered data, among which two sets are out of range with an Ag^+ /electron ratio
397 close to 2:1. Here the relatively high value for the Ag^+ release may be attributed to loss of
398 nanowire debris to solution, and these debris may have been included in the quantification of
399 silver. Over all the results suggest that the measure of quantity of charge obtained in the

400 corrosion experiment is a number representative of the amount of corrosion of silver in
401 AgNW films. For coated films, it is directly proportional.

402 Concerning the quantification of results of the commercial products containing silver, the
403 skiing goggle glasses released small amounts of dissolved silver (40.88 $\mu\text{g/L}$), comparable to



404

405 **Figure 4.** a) Silver concentrations (mean values) in the reactor solutions of the experiments
406 presented in Fig. 3.a. The high standard deviation values ($n= 5$) are related to the variable
407 qualities of the different plates used (see SI appendix, Figure S12). b) For individual samples,
408 correlation between quantity of electrons released (E_r) derived from current measurements by
409 potentiostat and dissolved silver from AgNW films (Ag^+) detected in solution by ICP-MS.
410 Coated films (bleu dots) show good linear relation between both parameters with a slope of
411 almost 1, while uncoated films (red dots) gave rise to more scattered data. Detailed
412 calculations of both parameters in SI appendix.

413

414 the levels obtained in the thick coated AgNW films of the present study. Interestingly, indium
415 was also released to solution (7.28 $\mu\text{g/L}$). EDS analyses suggest the presence of indium oxide
416 in the skiing goggle glasses.

417 In the case of silver antibacterial textile, the concentration of dissolved silver reached 4.57
418 $\times 10^4$ $\mu\text{g/L}$. The high specific surface area of the silver used as a coating of the textile fibers
419 may explain this very high release.

420 These first trials on commercial Ag containing household products demonstrate that the
421 corrosion method developed here allows obtaining a rapid estimate on the corrodibility of a
422 silver containing material and on the potential metal release. The application of the method to
423 the antibacterial textile shows that it can be used as well for macro-scale corrodible silver
424 containing compounds.

425

426 *3.4. Anthropogenic silver release to the environment and potential impacts*

427 When considering all categories of AgNW conductive transparent films investigated in this
428 study, the range of silver concentrations released from the AgNWs films ranged from
429 approximately 90 µg/L to 400 µg/L (0.83 µmol/L to 3.7 µmol/L). These concentrations can be
430 confronted to toxicity data. Ionic silver has been shown to bioaccumulate in various aquatic
431 organisms and to be highly toxic to bacteria, phytoplankton, and aquatic invertebrates and
432 vertebrates with toxicity threshold values typically around 0.2 µg/L (Croteau et al., 2011;
433 Davies, 1978; Farkas et al., 2010; US EPA, [https://www.epa.gov/wqc/ambient-water-quality-](https://www.epa.gov/wqc/ambient-water-quality-criteria-silver)
434 [criteria-silver](https://www.epa.gov/wqc/ambient-water-quality-criteria-silver)). These organisms have important roles in the trophic ecosystem as primary
435 producers and consumers, and adverse impacts of silver to these organisms could have
436 detrimental consequences to overall ecosystem health (Glibert, 2012; Vaughn, 2010).

437 The toxicity of ionic silver to humans depends on the type of cells that are exposed, the
438 liver cells being the most sensitive. According to the American Conference of Governmental
439 Industrial Hygienists (ACGIH, <https://www.acgih.org/>), the occupational exposure limit for
440 dissolved silver to prevent argyria is 0.01 mg/m³ (0.01 µg/L).

441 Overall these limits demonstrate that the silver released during the corrosion test of the
442 AgNW films is orders of magnitude above the levels acceptable for the natural environment
443 and living species, even in the case of a thick protective coating (90 µg/L), thereby they point
444 to the relevancy of this test.

445 Concerning anthropogenic input of silver to aquatic systems, Zhang et al. (2008) reported
446 concentrations of dissolved silver in the surface water of Tokyo Bay ranging from 6.5x10⁻⁴
447 µg/L to 1.7 x10⁻³ µg/L, a level also obtained for the surface waters of the Japan Sea. Deycard
448 et al. (2017) found average dissolved concentrations of 1x10⁻³ µg/L in river water of the “La
449 Réole site” in France. They also reported that the daily silver concentration in an urban

450 wastewater treatment plant located on the fluvial part of the Gironde estuary, ranged from
451 0.14 to 0.55 $\mu\text{g/L}$ depending on weekday and meteorological conditions.

452 Estimations of nanosilver environmental release are primarily based on modelling
453 approaches. Giese et al. (2018) estimated environmental concentrations of Ag-ENM arising
454 from medical applications to have reached 3.8×10^{-4} $\mu\text{g/L}$ in surface fresh waters in Germany
455 in 2017 and predicted an increase to 8.9×10^{-4} $\mu\text{g/L}$ for 2030. In sewage treatment effluents,
456 modelling calculations gave 1.89×10^{-2} $\mu\text{g/L}$ for 2017 and 3.06×10^{-2} $\mu\text{g/L}$ for 2030
457 respectively.

458 Silver released from AgNW films during the corrosion test may be put into the perspective
459 of current background levels of Ag in anthropogenically influenced waters. Indeed the 5-10
460 mL of solution in the electrochemical cell would have to be diluted by an average factor of
461 2000 before “disappearing” in the general background. The diversification of (nano)silver
462 containing products and the increase in their production will irrevocably increase the Ag
463 background concentrations in natural systems and affect water quality.

464 The human body may come in direct contact with silver from anthropogenic source.
465 Deycard et al. (2017) reported that Ag concentrations in a typical household personal care
466 product (deodorant) labeled as containing Ag, range from 0.2 to 0.4 mg/kg of solution (200
467 $\mu\text{g/L}$ to 400 $\mu\text{g/L}$). These concentrations are within the interval of values generated during our
468 corrosion test. The comparison is appealing because AgNW TCF are predestined to be in
469 contact with skin. Thus, silver released from AgNW TCF may be significant compared to
470 current silver levels in contact with the body.

471

472 *3.5. Relevance of the developed corrosion test*

473 The experimental results obtained in this work on silver corrosion in AgNW films allow us
474 to estimate an average silver corrosion rate of about 3.7×10^{-10} g/s (Calculation details in SI

475 appendix, Table S3), which is a factor 30 larger than the rate measured for the natural
476 dissolution of a noble silver foil in water saturated with air (Graedel, 1992). This comparison
477 highlights the strength of the method developed here, where a corrosion potential, slightly
478 enhanced compared to natural conditions, leads to a fast and easily measurable response of the
479 investigated sample. This method is therefore well adapted to assess the risk of metal release
480 from everyday consumer products to their immediate environment (skin, corporal fluids,
481 effluent waters, aquatic systems).

482 The potential application fields of the accelerated release test are wide, however the field of
483 biosensors appears as a very promising one because the use of wearable electronic sensors
484 containing metallic and in particular nanowire silver is growing and because in these devices,
485 the film electrodes are often located in humid environment and in direct contact with the skin.
486 Moreover biocompatible capping agents e.g. citrate are often used in antibacterial Ag-ENMs,
487 which can enhance silver solubility (Liao et al., 2019).

488 An important aspect also is that the method can be applied at any time in the life cycle of
489 the AgNW film. Nowack and Mitrano (2018) discuss the importance of performing aging-
490 release tests in ENM-nanoproducts during use rather than in pristine materials, as consumers
491 and the environment are mostly exposed to aged and transformed nanomaterials (Baun et al.,
492 2017). The method may play a role in predicting the silver flux from household products,
493 biosensor products and personal electronics containing nano-silver (Steinhäuser and Sayre,
494 2017) during life-time and at end of life. In the case these products come in contact with the
495 environmental water compartment, the method will again provide valuable data for flux
496 estimates.

497 While experiments presented in this work on AgNW coated films have been conducted with
498 a polysiloxane coating (anti-scratch varnish AE12®), more research needs be perform with
499 AgNW films with other matrices, other coatings, in particular hydrophobic polymers like

500 epoxy or new materials such as optical adhesive or reduced graphene oxide layers, is
501 necessary to work out the method limitations. Reference AgNW TCF materials would also
502 need to be developed with known toxicological characteristics.

503 The current lack of standard methods to quantify the risk of exposure of ENM enabled
504 devices to the environment, underline the importance of developing the accelerated corrosion
505 method into a standard method for quantifying the releasability of metals from conductive
506 thin films. The way forward will be to constitute a data base for reference conductive films to
507 which new materials could be compared.

508

509 **4. Conclusions**

510 In this work, we developed an electrochemical method to evaluate the potential corrosion
511 activity of silver in nanowire transparent conductive films (AgNW TCFs), with or without
512 coating (polysiloxane varnish AE12 ®), and the possible release of ionic silver. We have
513 demonstrated that there is a consistent link between the corrosion current response obtained
514 from coated AgNW TCFs, Ag⁺ release and the coatings' characteristics. The corrosion current
515 in each experiment is transformed into quantity of charge, a single number representative of
516 the corrodibility of a material. This corrosion indicator is established quickly, 20 minutes are
517 sufficient for a diagnostic result. The method is thus seen as an accelerated corrosion test,
518 with speed being a significant advantage compared to classical aging studies. Additionally,
519 this method is free from harmful reagents and is low power consumption.

520 Previous works mainly focused on technical quality control of AgNW transparent
521 electrodes, in particular on lifetime stability of the devices. To our knowledge, this is the first
522 investigation of the corrodibility of a conductive nanomaterial under aqueous conditions, in
523 order to assess the risk of metal release to users and the environment.

524 A significant result obtained with the accelerated corrosion test is the fact that protective
525 coatings of AgNW films do not systematically provide full protection against corrosion of
526 silver and the release of ionic silver to outside the material. Our results demonstrated that
527 even a thick 5 μm layer of protective polysiloxane coating could not stop AgNW corrosion
528 completely, still leaving a risk of silver (Ag^+) release.

529 The accelerated corrosion method is promising because it tests the degree of isolation of a
530 material by the possibility of electron flow. The measure of corrodibility depends not only on
531 the presence of (nano) silver but also on textural parameters, in particular the degree of
532 dispersion of the particles in the material and the characteristics of protective coatings. We
533 suggest that the accelerated corrosion method could be elevated to the level of a standard
534 material quality control method to quantify the risk of silver release by corrosion from
535 (nano)silver containing products.

536 The method is not strictly limited to the study of AgNW TCFs, and can be adapted to
537 products containing other oxidisable conductive nano-materials, in particular those with
538 oxidation potential below that of water. Several technology-critical elements (TCE),
539 increasingly applied as ENMs, with application fields where toxicology limits are even less
540 well explored, could be targeted.

541

542 **Abbreviations**

543 AgNW: silver nanowires

544 Argyria: is a condition caused by excessive exposure to chemical compounds of the
545 element silver, or to silver dust.

546 ENMs: engineered nanomaterials

547 ITO: indium tin oxide

548 Nanoproduct: product containing nanomaterial

549 PEDOT:PSS : poly(3,4-Ethylenedioxythiophene):poly(StyreneSulfonate)

550 PEN: polyethylene naphthalate

551 PTFE: polytetrafluoroethylene

552 PVA: polyvinyl alcohol

553 PVP: poly-vinylpyrrolidone

554 SHE: standard hydrogen electrode

555 TCF: transparent conductive film

556 **Acknowledgements**

557 This study was conducted in the framework of the project NanoWIR2ES (Nanowire
558 Intelligent Re-Design and Recycling for Environmental Safety) supported by the European
559 Union ERANET-SIINN program (European Research Area Network Safe Implementation of
560 Innovative Nanoscience and Nanotechnology) and was funded by the « Region Hauts de
561 France ». Many thanks to Guillaume Bai (University of Lille) who conducted water contact
562 angle measurements on polysiloxane resin, and Sandra Ventalon (University of Lille) for her
563 help in the spectroscopic observations. We greatly appreciated working with Christophe
564 Vermander (Ecole Centrale de Lille) who realized the electrochemical reactor and Jean
565 Claude Bruyere who helped elucidating the chemical properties of polysiloxane AE12.

566

567 **Appendix A. Supplementary data**

568 Supplementary data contain complementary information regarding method and results: table
569 of large plates used for preparation of AgNW films, description of coating material and
570 sample preparation, effect of ionic strength on current generation, details on calculation of
571 quantity of charge, experiment results under fixed electrolyte volume, images showing NW
572 displacement on uncoated films, images highlighting characteristic features of natural

573 alteration (artifacts) on NW films, effects of NW-network density and NW diameter on
574 current, description of silver-chloride nanocubes and EDS spectra, table of stability constants
575 for silver species, model calculations for aqueous silver speciation, water contact angle
576 measurement on control samples, AFM roughness measurements on coated AgNW films,
577 dissolved silver after micro and ultrafiltration, comparison between unaltered and altered
578 large plates, conversion of Ag⁺ concentrations and electric current generated to a common
579 unit (nmol.cm⁻²), details for calculations of corrosion rates, supplementary images illustrating
580 corrosion signatures on AgNWs after corrosion test.

581

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