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1 **Transparent Heaters: A Review**

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5 **Keywords:** transparent electrode, Joule heating, film heater, composite, stability

6

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14

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16 **Short summary**

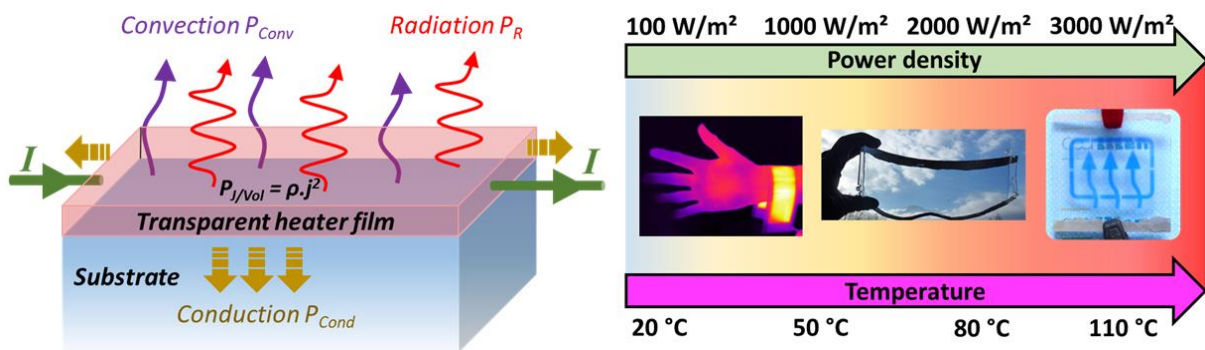
17 Transparent heaters (TH) have attracted intense attention from both scientific and industrial
 18 actors due to the key role they play in many technologies, including smart windows, deicers,
 19 defoggers, displays, actuators and sensors. While transparent conductive oxides have
 20 dominated the field for the past five decades, a new generation of THs based on nanomaterials
 21 has led to new paradigms in terms of applications and prospects in the past years. Here we will
 22 review the most recent developments and strategies to improve the properties, stability and
 23 integration of these new THs.

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26 **Graphical abstract**

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31 **1 Introduction**

32

33 Transparent heaters (THs) are visually transparent devices that contain electrically conductive
34 layers. When an electrical current flows across the transparent heater, it generates heat thanks
35 to the Joule effect. This heat can be efficiently used in many devices. Consequently, numerous
36 applications are concerned by THs, and the associated TH market is growing fast, comprising
37 many types of devices (smart windows, deicers, defoggers, displays, thermotherapy pads,
38 sensors...) for different industrial sectors (transport, buildings, healthcare, sport...). For
39 instance, THs can provide the warmth required to extend the operating temperature of liquid
40 crystal displays (LCDs) in cold environments or can increase the temperature for anti-fogging
41 systems, anti-icing, deicing of optics and optical displays (very useful for transportation). Other
42 applications include the heating of specific industrial processes, of microfluidic chips, of kiosks
43 and handheld devices.^[1] Display technology and smart windows (used in transport or for
44 interior architecture) are among the fastest growing markets related to THs. Importantly,
45 defrosting windows in airplanes enables high-altitude flying.^[2] Smart windows can reduce
46 energy loss in buildings, which currently account for over 40% of the energy consumed. This
47 works thanks to special functional coatings which can regulate solar energy in response to heat
48 (thermochromic material).^[3,4] This heat can be generated by THs within smart windows.^[5]
49 While the required optical transparency depends upon the specific application, in this review
50 we have considered THs having an optical transparency of at least 50%.

51 The fast control of temperature via the applied current or voltage makes THs a generally better
52 choice when compared to conventional heating elements. This is enabled by the small thermal
53 inertia of thin TH films.

54 The only technology used for TH before 1995 was based on transparent conductive oxides
55 (TCOs), which were also broadly used as transparent electrodes in many applications including
56 photovoltaics^[6], smart windows^[7], efficient lighting^[8] or displays.^[2,7,9,10] The three main TCO

57 materials are indium tin oxide (ITO)^[11–13], the most well-known and used TCO, fluorine-doped
58 tin oxide (FTO)^[14,15] and aluminum-doped zinc oxide (AZO).^[16–19] TCOs are generally
59 degenerately-doped n-type semiconductors which exhibit a high electrical conductivity of 10^3 -
60 10^4 S/cm.^[9] They are often fabricated as thin films of approximately 300 nm thickness in order
61 to show high transparency (~90%). While TCOs can exhibit good or even excellent
62 performances in terms of the trade-off between electrical conductivity and optical transparency
63 in the visible range, their two main drawbacks concern their non-flexibility (due to their ceramic
64 nature) and their intrinsic low optical transmittance in the near-infrared (NIR) spectrum due to
65 plasmonic absorption^[13,20]. Therefore, great attention has been devoted to flexible and
66 transparent electrodes^[21] or heaters for three main reasons: i/ the emergence of new-generation
67 devices having flexible or nonplanar substrates, ii/ the potential scarcity of indium for ITO and
68 iii/ the lack of transparency in the NIR. For some applications, even flexibility is not sufficient
69 since stretchability could be a prerequisite, like for the integration of THs within wearable
70 electronics.^[22] For example, flexible but also stretchable THs can be used in thermotherapy^[23,24],
71 a popular treatment in physiotherapy which is particularly useful for the treatment of joint
72 injuries and pain. For such applications, THs should also be soft and thin (and therefore light)
73 so that comfort is not compromised.

74 It is also worth noting that even for non-flexible devices, we are looking for high throughput
75 fabrication methods which are compatible with an economically viable technology, like the
76 roll-to-roll (R2R) process. Indeed, R2R is a fast processing method associated with little or no
77 loss of material, and which requires that both substrate and active layers be flexible.^[25,26]
78 Therefore TCOs themselves are not compatible with such low-cost methods, except when
79 integrated as very thin films with other materials such as oxides or metals, and thus alternative
80 THs need to be developed.

81 Several emerging materials have recently been investigated for TH applications, including
82 carbon-based nanomaterials, and mainly carbon nanotubes (CNT)^[27] and graphene^[28]. These

83 new materials are rather cheap and abundant and could therefore follow the fast-growing
84 industrial demand. Moreover, THs made of these building blocks are flexible and can be
85 processed in solution. In parallel, since 2009 metallic nanowire (MNW) networks have started
86 to be more systematically investigated, notably following the seminal articles on: i) the
87 synthesis of MNWs by the groups of Sun^[29] and Wiley^[30–32], among others; ii) the study of the
88 physical properties of MNW networks by Coleman's group^[33,34]; and iii) the integration into
89 efficient devices by Pei's group.^[35,36] Several recent reviews have summarized the main
90 properties, challenges and integration of MNW networks^[20,37–41]. The first article showing that
91 silver nanowire (AgNW) networks could act as efficient THs was published in 2012 by
92 Simonato's group.^[42] As shown below, this ground-breaking paper was followed by many other
93 studies focused on the physics of THs based on MNW networks^[43], on the integration of this
94 type of TH into various devices^[22,44,45] as well as on a better understanding and enhancement
95 of these THs.^[46–48] More recently, great progress has also been reported on conductive
96 polymers which can now be considered as very efficient materials for THs.^[49] For instance,
97 Simonato's group^[50] has also reported the very first efficient TH exclusively based on thin
98 films of conducting polymers.

99 While many reports show an intense research activity on each of these TH technologies, there
100 is also active research on multi-layered materials or nanocomposites which can combine the
101 advantages of different materials. For instance, Ko et al. showed that high-performance and
102 flexible R2R sputtered ITO/Ag/ITO multilayers can exhibit a high optical transmittance
103 (88.2 %), low sheet resistance (3 Ω /sq) and can be efficiently integrated in a TH device.^[51]
104 Similarly, Park et al. reported that ITO/Cu/ITO multilayer materials can also show promising
105 electrical and optical performances and good TH integration.^[52] The different technologies will
106 be thoroughly discussed in section 3 of this review.

107 The main scientific and technological features associated with THs can be listed as follows:
108 thermal response time, steady state temperature, homogeneity, mechanical properties (under

109 bending and/or stretching tests), cycling/thermal/electrical/environmental stability including
110 ageing, electrical and optical properties, fabrication process of the TH (the temperature being a
111 potential issue for some applications), the material used, TH size and, finally, the overall
112 fabrication cost, including both materials and processes.

113 Expected requirements associated to the TH can drastically differ depending on the targeted
114 applications. For instance, smart windows, windscreens or displays require that the THs and
115 their associated substrates exhibit high optical clarity, i.e. high optical transparency and low
116 haziness (defined as the ratio between diffuse and total transmittance of light). Optical
117 engineering related to THs notably concerns matching the optical index to improve reflection
118 and transmission properties in the desired wavelength band (i.e. visible and/or NIR spectra).
119 The thermal response time is also a crucial parameter. The targeted steady state temperature of
120 THs can be very different depending on the application. For smart windows applications, the
121 thermochromic transition (i.e. metal-insulator transition) associated to hybridized
122 VO₂/Graphene is about 60 °C^[53]. A low temperature is generally required for de-icing or
123 defogging uses (below 30 °C). Some other applications need much higher temperatures, like
124 fast defrosting in automotive or for gas sensors (see section 4 of this review). In these cases the
125 chosen material for the TH should exhibit a very good thermal and electrical stability. TH
126 stability can be a serious issue, especially when numerous cycles are foreseen during the
127 lifetime of the device. It is worth noting that stability is related to several other aspects,
128 including potential cycling/thermal/time/electrical/environmental issues. These crucial aspects
129 will also be addressed in this review. The homogeneity of THs plays a key role for many
130 applications. For example, this is essential for eye comfort when THs are used in windscreens,
131 while hot spots can potentially be at the origin of the TH degradation.^[54]

132 As for all industrial devices, cost is overwhelmingly important to propel the commercialization
133 and large industrial production (e.g., adding a TH within a ski or motorcycle helmet visor should
134 only cost a few euros), with only a handful of exceptions like spatial applications.

135 This review is organized as follows. The main physical mechanisms associated with THs are
136 presented in part 2.1, as well as simple physical models developed to better understand TH
137 behavior. The main experimental methods currently used to investigate and explore the critical
138 properties of THs will be described in part 2.2. Stability issues are thoroughly considered in
139 section 2.3, from their physical origin to the solution for stability enhancement. Each TH
140 technology (i.e. associated to specific material) is detailed. A thorough comparison and critical
141 discussion of the different active materials are reported in section 3. Part 4 focuses on the
142 integration of THs in different devices with specific associated requirements and performances.
143 Finally, part 5 gives an overview of the main challenges that lie ahead and the main prospects
144 related to THs in terms of better physical understanding, better performances and stability, as
145 well as their future integration into industrial devices.

146

147 **2 Principle of transparent heaters (THs):**

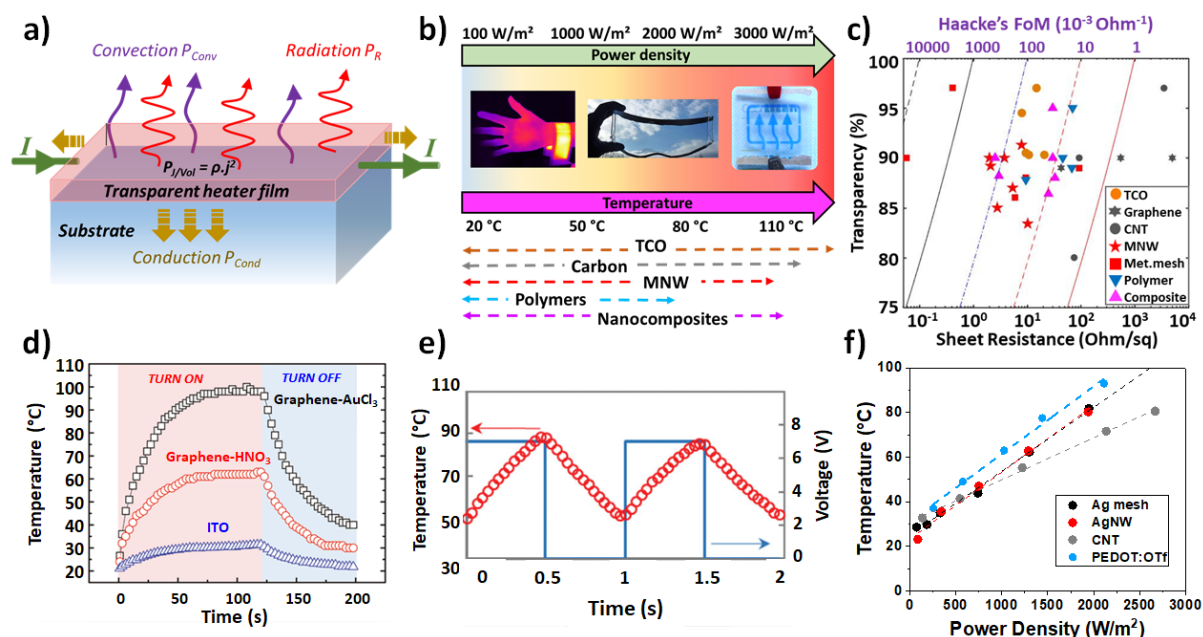
148 **2.1 Introduction to the thermal physics of THs**

149

150 As stated above, THs are based on the Joule effect. Joule's law, experimentally demonstrated
151 by J.P. Joule (1818-1889), states that when an electrical current I crosses a homogeneous
152 conductive material with an electrical resistance R , the amount of heat released is equal to I^2R
153 per unit of time. The power dissipated in the material is directly related to the achieved steady-
154 state temperature, through a balance between the Joule effect and heat loss. These thermal losses
155 are schematically presented in **Figure 1a**: they correspond to the total heat transfer from the TH
156 and are associated to three main physical origins: i/ thermal conduction to the substrate or
157 through any conducting connections, ii/ convection to the surrounding air and iii/ radiation
158 emitted from the hot surfaces. Figure 1b exhibits some TH applications (medical, defogging,
159 thermochromic), with characteristic values of temperature and areal power density. Several TH

160 technologies do exist, and their corresponding temperature ranges are roughly presented in
161 Figure 1b in dashed lines. That being said, these temperatures depend upon the TH fabrication
162 process and the experimental conditions under which the TH is used for a given application.
163 Figure 1c reports the typical performance of the main TH technologies in terms of optical
164 transparency Tr (the substrate transparency being subtracted) versus the electrical sheet
165 resistance R_{sh} . The ongoing efforts by the community are focused on fabricating THs which
166 are, simultaneously, as transparent and as conductive as possible (i.e. with a low sheet
167 resistance). There is a trade-off between these two properties since for a homogeneous
168 transparent conductive layer, the thicker the layer the lower the sheet resistance, but also the
169 lower the optical transparency. This trade-off can be approached thanks to a figure of merit
170 (FoM). For transparent electrodes (TEs), two main figures of merit have been proposed thus
171 far. The first one was derived by Haacke et al. in 1976 who proposed to consider the ratio
172 between the 10th power of the total optical transmittance Tr divided by the sheet resistance R_{sh} :
173 Tr^{10}/R_{sh} .^[55] Haacke's FoM is very often used when dealing with transparent electrodes
174 applications (such as photovoltaic or displays) but also for TH investigations. Another figure
175 of merit was later derived by Coleman's group, who considered the ratio between the electrical
176 conductivity and the optical conductivity (equal to the optical absorption coefficient divided by
177 the free space impedance Z_0 (the latter is equal to: $1/(c \cdot \epsilon_0)$, where c is the speed of light and ϵ_0
178 the permittivity of free space).^[33] Both these FoMs are used as guides for comparing TEs and
179 THs. Although they make physical sense for homogeneous and continuous thin layers, they
180 have to be considered with more caution for non-homogeneous layers **such as CNT networks,**
181 **metallic grids, or MNW networks.** For example, in the case of very long 1D conductive objects,
182 a very high FoM could be obtained even if it does not present high homogeneity or usefulness
183 for device integration. Different values of Haacke's FoM are plotted in Figure 1c, showing that
184 there is a good variety of TH technologies that exhibit very good electrical and optical
185 properties, and that are therefore well suited for TH integration. Other parameters of TH

186 applications have to be taken in consideration as well; for instance, graphene appears to be less
 187 conductive and therefore it will not be used alone for fast TH operation, as discussed in section
 188 3.5.4. **Chen et al. reported recently copper grid TH with an outstanding Haacke's FoM over**
 189 **$7820 \cdot 10^{-3} \Omega/\text{sq}$ (see Figure 1c), and a fast heating rate at low voltage.^[56] This clearly illustrates**
 190 **the efficiency of such technology as TH.**
 191 Figure 1d exhibits the time-dependent temperature of graphene-based THs with two different
 192 doping agents, and an ITO-based TH for the sake of comparison.^[57] During the "ON" voltage
 193 state, the classical time-dependent behavior shows a linear increase at first, followed by a
 194 saturation to a steady-state temperature. The three different materials used have different initial
 195 R_{sh} and therefore exhibit different steady-state temperatures for the same applied voltage (here
 196 12 volts).^[57]



197
 198 **Figure 1.** Main features of THs. a) Schematic of a TH: the thin TH is crossed by an electrical current,
 199 leading to heat production thanks to the Joule effect. A steady state is reached once this generated heat
 200 is equal to the sum of the heat losses shown with different colors. b) Main application domains of THs
 201 versus areal power density or temperature required. The arrows below represent roughly the typical
 202 maximum steady-state temperatures for the main TH technologies. c) **Optical transparency versus sheet**
 203 **resistance diagram for different TH technologies based on: transparent conductive oxides (TCO)^{[14,33,58-}**
 204 **$60]$, carbon nanotubes (CNT)^[27,33,61], graphene^[57,62,63], metallic nanowire (MNW) networks^[64-70], metallic**
 205 **grids-meshes^[56,71-76], conductive polymers^[49,50,77,78], nanocomposites^[22,48,51,79-81]. The dashed lines**
 206 **correspond to different values of Haacke's FoM: 10000, 1000, 100, 10, 1 times $10^{-3} \Omega/\text{sq}^{-1}$.** d) Time-
 207 dependence of temperature for graphene-based and ITO-based THs, showing the presence of a

208 transitional and steady-state regimes. The optical transmittance of ITO is 95.6% and those of graphene-
 209 based THs are 88.5% and 87.5%, respectively for AuCl₃ and HNO₃ doping protocols. Reproduced with
 210 permission. ^[57] Copyright 2011, American Chemical Society. e) Time-dependence of temperature
 211 during voltage cycling showing a very fast thermal response when a TH (here composed of a carbon
 212 nanotube network) is deposited on a very thin substrate (12 Ω.m thick mica)^[61], in agreement with eq.4.
 213 Reproduced with permission.^[61] Copyright 2017, AIP Publishing f) Areal power density dependence of
 214 the stabilized temperatures measured for different TH technologies: a linear dependency is generally
 215 observed at least for temperatures lower than 100 °C (data for TH based on AgNW^[46], Ag mesh^[82],
 216 CNT^[61], PEDOT:OTf^[50]). The slope appears rather similar for the different TH technologies.

217
 218 Sorel et al.^[43] gave a comprehensive and thorough description of the theory of Joule heating in
 219 a TH in general, and focused in more detail on THs based on silver nanowire networks. But
 220 similar approaches can also be found for other types of TH technologies, such as graphene^[83]. In
 221 general, the main key parameters for a TH are the steady-state temperature T_{stab} , and the time
 222 needed to approach T_{stab} . Most THs are supposed to reach the desired temperature by using a
 223 rather low voltage (< 12 V for standard uses) and after a relatively short response time (i.e. from
 224 a few seconds to a few minutes).

225 Considering that the temperature is uniform across the whole TH, the energy balance at a given
 226 time t can be written as follows (conduction losses due to external parts of the system are
 227 neglected)^[43]:

$$228 \quad I^2 R = (m_1 C_1 + m_2 C_2) \frac{dT(t)}{dt} + A(h_1 + h_2)(T(t) - T_0) + \sigma A(\varepsilon_1 + \varepsilon_2)(T(t)^4 - T_0^4) \quad (1)$$

229 For each parameter, the indexes 1 and 2 correspond to the TH and the substrate, respectively;
 230 the instantaneous sample temperature is $T(t)$, while the ambient temperature is T_0 . In eq. 1, the
 231 term on the left is the dissipated heat per unit of time. The first term on the right is the sum of
 232 the heat per unit of time associated to the TH and to the substrate (transported via thermal
 233 conduction). This heat is responsible for the temperature elevation of the sample through the
 234 specific heat capacities C , with m_1 and m_2 being the mass of the TH itself and of the substrate
 235 respectively. The second term represents the heat losses per unit of time by convection, with h_1
 236 and h_2 being the convective heat-transfer coefficients and A the film area, assumed to be equal
 237 to the substrate area. Finally, the third term stands for the heat losses by radiation, where σ is

238 the Stefan-Boltzmann constant and ε_1 and ε_2 the emissivity of the TH and of the substrate,
 239 respectively. Considering small temperature rises, allowing a linear expansion of eq.1 (the non-
 240 linear term associated to radiation losses being neglected) and with the hypothesis that the TH
 241 has a much lower heat capacity compared to the substrate ($m_1C_1 \ll m_2C_2$), the energy balance
 242 then has the following analytical formula^[43]:

$$243 \quad \Delta T(t) = T(t) - T_0 \approx \frac{1}{\alpha} \frac{I^2 R}{A} \left[1 - \exp\left(-\frac{\alpha}{m_2 C_2 / A} t\right) \right] \quad (2)$$

244 where α is the heat transfer constant, which takes into account the parameters of heat losses
 245 expressed as follows:

$$246 \quad \alpha = (h_1 + h_2) + 4(\varepsilon_1 + \varepsilon_2)\sigma T_0^3 \quad (3)$$

247 Eq. (2) shows that there is a transitional state for a short time, i.e. for a small t compared to the
 248 characteristic time τ , while for times much larger than τ , a steady-state temperature is achieved
 249 and the saturation temperature is then equal to: $\frac{1}{\alpha} \frac{I^2 R}{A}$. The expression of τ is given by:

$$250 \quad \tau = \frac{m_2 C_2}{\alpha A} = \frac{\rho_{sub} t_{sub} C_{sub}}{\alpha} \quad (4)$$

251 where ρ_{sub} , t_{sub} and C_{sub} are, respectively, the density, thickness and specific heat (per unit of
 252 volume) of the substrate. After a time $t=\tau$, the temperature reaches 63% of the saturation
 253 temperature. Another characteristic time, called the response time, is also often used in the
 254 literature: it is defined as the time required to reach 90% of the steady-state temperature, its
 255 value being equal to $\text{Ln}(0.1) \tau$, i.e. 2.3τ .

256 The existence of both transitional and steady-state temperatures is validated by experimental
 257 observations, as shown in Figure 1d. τ is generally found to be between 10 and a few hundreds
 258 of seconds for the great majority of experimental reports. As a first approximation, this value
 259 does not depend much on the material that composes the TH. Accordingly, this range of τ
 260 values was observed for THs composed of AgNW networks^[45], CNT networks^[27], TCO^[84],
 261 conductive polymers^[50], electrospun nanofibers^[76,85] or graphene^[86]. For efficient THs, the τ

262 value mainly depends on the characteristics of the substrate: the thinner the substrate, the shorter
263 the characteristic time. For example, the steady state temperature was achieved within 10 s
264 when graphene films were deposited on a 50 μm thick polyimide (PI) film, while it took 80 s
265 using 1 mm thick quartz as a substrate^[86]. This is coherent with equation (4). For very small
266 substrate thicknesses τ can be very short too. Kim et al. demonstrated, as depicted in Figure 1e,
267 that the use of single-walled carbon nanotubes (SWNTs) on a very thin polymeric substrate (12
268 μm thick) leads to a fast response: a temperature of 100 $^{\circ}\text{C}$ could be reached within 1 s with an
269 input voltage of 7 V^[61]. Ke et al. used the same idea and obtained similar results on Al-doped
270 zinc oxide deposited on 25, 65 and 100 micron thick mica substrates^[60].

271 According to equation (2), the steady-state temperature elevation, ΔT_{stab} , appears to be directly
272 proportional to the applied areal power density and, as a first approximation, does not drastically
273 depend on the TH type. Figure 1f presents the areal power density dependence of the stabilized
274 temperatures measured for different TH technologies and demonstrates this trend. A linear
275 dependency is generally observed (data for TH based on AgNW^[46], Ag mesh^[82], CNT^[61],
276 PEDOT:OTf^[50]) at least for temperatures lower than 100 $^{\circ}\text{C}$. The slope appears rather similar
277 for the different TH technologies. These slopes depend on the different thermal losses which
278 vary also according to the surface properties of the TH thin film and the substrate^[60]. The
279 different thermal losses are convection, infra-red radiation and thermal conduction outside the
280 TH itself (through the TH substrate/holder or the electrical connecting wires). Several
281 investigations have tried to estimate the contribution of each thermal loss mechanism, which in
282 turn depends on the substrate, temperature and TH material used. Sorel et al. discussed their
283 dependence versus AgNW network density and showed that there is an increase in convection
284 losses for denser networks which is caused by a higher surface roughness and higher internal
285 area^[43]. The thermal conductivity and thickness of the substrate play a key role for thermal
286 conduction losses. In general, radiative losses are negligible compared to conductive and/or
287 convective losses, at least at low temperatures. Conversely, for high temperatures the radiative

288 losses can contribute significantly, and the linear approximation is not valid anymore. The
289 linear dependence between the steady-state temperature and the areal power density is therefore
290 not valid anymore. For instance, Ji et al. reported the fabrication of highly-stable THs based on
291 ultra-long copper nanofiber networks that can be heated up to 800 °C^[87]. In this case, the steady-
292 state temperature versus heat power does not show a linear dependence in the entire temperature
293 range (as reported in the supplementary information of Ji et al).^[87] Interestingly, comparing the
294 same TH in air and in vacuum conditions allows us to disentangle convective losses from
295 conduction and radiation losses. Lagrange et al. performed similar experiments on AgNW
296 networks deposited on glass^[46]: in air and in vacuum the temperature elevations increase
297 linearly with the areal power density, but with different slopes. The difference between these
298 two slopes (23.8 and 28.1 W.m⁻².K⁻¹ in vacuum and in air, respectively) allows us to deduce
299 convective thermal losses: $h_{convective}$ could be estimated as 4.3 W.m⁻².K⁻¹.^[46] Another interesting
300 discussion was also reported by Kang et al. regarding the influence of the CNT film density on
301 the different types of heat-transfer losses.^[88] This can be understood through the heat-transfer
302 losses that are directly related to the porous morphology of the CNT network.^[88]
303 One can already classify THs into two different categories: on one side, the homogeneous layers
304 like transparent conductive oxides (TCO), graphene, multilayers (composed of a thin metal
305 surrounded by oxide layers) or conductive polymer films; on the other side, networks composed
306 of carbon nanotubes, metallic nanowires, meshes and fibers. While the first category is
307 supposed to heat homogeneously the whole TH surface, the second category can induce local
308 heating due to its non-homogeneous nature, if heat does not diffuse along both the active
309 material and/or the substrate quickly enough^[54]. These hotspots can induce local degradation
310 within the TH and are therefore an issue to be dealt with. Das et al. investigated scaling in self-
311 heated percolating networks and concluded that hotspot clustering appears to be a mechanism
312 analogous to crystallization physics^[89]. The potential presence of hotspots will be discussed in
313 this review, since their presence can lead to TH instability. In brief, the thermal stability of the

314 TH can be limited to the TH itself (e.g. degradation of the conductive polymer or morphological
315 instability of silver nanowires^[90]) or to the substrate as well. Specifically, for polymeric
316 substrates or low-quality glass substrates, heating can lead to local melting of the polymer or
317 cracking of the glass substrate. For instance, Maize et al. recently used the thermo-reflectance
318 technique to observe “super-Joule” heating hotspots in graphene and AgNW networks^[91], while
319 the latter would have appeared homogeneous using a macroscopic infrared technique. This
320 emphasizes the importance of spatial resolution in temperature observations and this point,
321 among others, is discussed in the following section devoted to the experimental methods used
322 to investigate the main properties of THs. It is worth mentioning that industrial needs require
323 that a good heater should exhibit uniform thermal distribution over the heating area and achieve
324 the target temperature often with a low voltage (i.e. below 12 V).

325

326 **2.2 Experimental methods to investigate the main properties of THs**

327 This section aims at introducing the main properties of THs and the experimental methods used
328 to investigate them. Generally speaking, a TH is considered efficient if it shows low electrical
329 resistance, high optical transmittance at least in the visible range, a controllable heating rate,
330 good stability and a low haze factor. We will first focus on electrical resistance and optical
331 transparency. Then, we will present the methods to investigate the basic operating modes of a
332 TH, the heating performances, which are particularly studied by temperature measurements at
333 different length scales. This enables us to measure characteristic features like the heating rate
334 and the relationship between temperature and areal heat power density. Regarding the
335 temperature, there are several ways to measure it through direct contact or contactless means,
336 and with different spatial resolutions, as illustrated below. Since the market appeals prompt
337 research for flexible (or even stretchable) TH, the methods to investigate their mechanical
338 properties are also discussed. Thermal, electrical, humidity and/or mechanical stresses are also

339 reviewed. Finally, other TH features like haze factor, adhesion and roughness are briefly
340 described, as well as their experimental investigation.

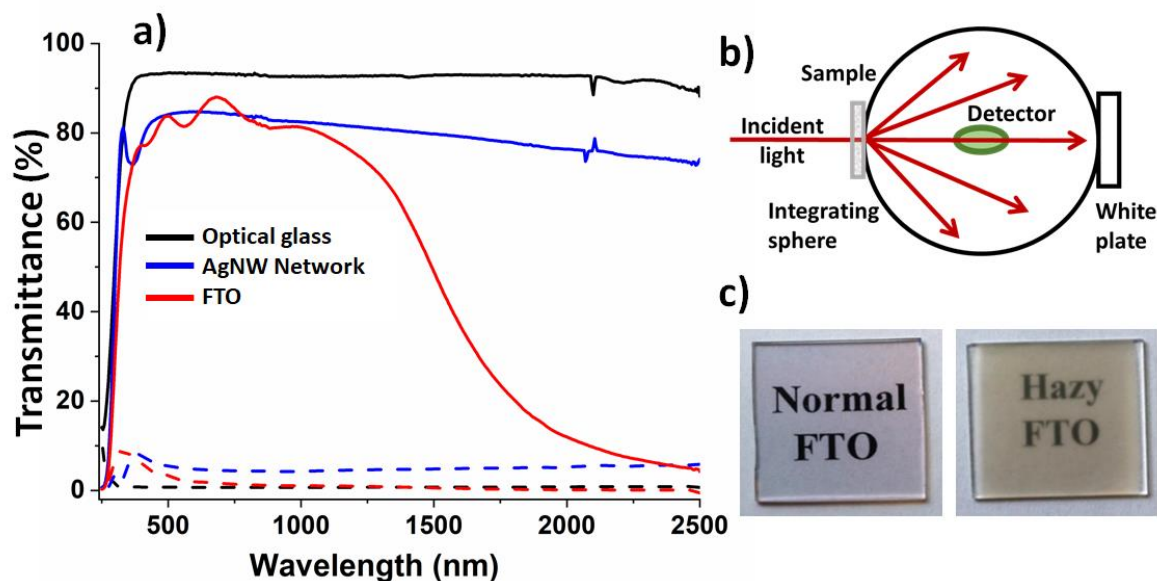
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342 **Electrical properties.** Electrical resistance is a key property of THs, and is evaluated using
343 several experimental methods. The sheet resistance R_{sh} (in Ω/sq) is traditionally used to
344 characterize uniform thin films, since it provides a direct and local measurement of electrical
345 properties, independent of specimen size. The four-point probe method allows a precise
346 measurement of R_{sh} since it eliminates the contributions of electrical wiring and contacts to the
347 global electrical resistance.^[92] This method is generally performed for emerging **Transparent**
348 **Conductive Materials (TCMs)** such as thin films or metallic nanowire networks, despite being
349 a direct contact method which can induce local damage. This electrical measurement is very
350 valuable for estimating the electrical homogeneity of a sample by measuring its electrical
351 performance in many different areas. As a first approximation and for a homogeneous layer,
352 R_{sh} is equal to the ratio between electrical resistivity and layer thickness, the latter being often
353 measured by an electronic microscope, a profilometer, Atomic Force Microscopy (AFM) or an
354 ellipsometer. Basic two-point probes can also provide the electrical resistance on samples. In
355 general, two parallel electrodes at opposite sides of the specimen are fabricated using silver inks
356 or metallic layers deposited by evaporation or sputtering. This two-probe method is generally
357 used to follow in-situ the electrical resistance measured during voltage or thermal ramps^[46,90].
358 For a homogeneous square layer with good electrical conductivity, the 4-probe and 2-probe
359 methods are expected to provide similar results. Another tool to investigate electrical
360 homogeneity is the one-probe electrical mapping, which draws up a cartography of voltage
361 distribution.^[93] **In addition, terahertz spectroscopy has been used for non-contact measurement**
362 **of the conductance of AgNW networks.**^[94]

363

364 **Optical properties.** A critical feature of THs is their optical transparency. As shown in **Figure**
365 **2a**, TCOs like FTO exhibit a very good transparency in the visible spectrum (390 to 700 nm).
366 However, their optical transmittances decreases dramatically in the NIR spectrum due to
367 plasmonic absorption (as described in section 3.1). Emerging TCMs such as metallic grids, or
368 metallic nanowire and CNT networks, allow the incident light to be transmitted through the
369 non-covered empty substrate spaces, and thus they remain transparent to a great extent in the
370 whole VIS-NIR spectrum. The transmittance of an AgNW network is shown in Figure 2a: this
371 network is still very transparent in the NIR region. In the case of THs, most applications are in
372 the visible range, which explains why most reports present only visible light measurements.
373 Total transmission can be measured precisely by UV-visible-NIR spectrophotometry with an
374 integrating sphere, as schematically depicted in Figure 2b. There are also small and handy
375 instruments like tint meters, which provide transparency values at a certain visible wavelength,
376 usually 550 nm (light wavelength for maximum efficiency of human eyes). Generally speaking,
377 the optical transparency is either reported in literature at this wavelength of 550 nm or averaged
378 over a typical range of 370-700 nm (i.e. the visible range), but unfortunately it is not always
379 reported whether authors refer to specular (i.e. direct) or total transmittance. The measurement
380 of diffuse transmission is of crucial importance. It is generally expressed through the haze
381 factor, defined as the ratio between the diffuse and total transmittances (Figure 2b). Figure 2c
382 shows a typical example of a low and a highly diffuse/hazy FTO. The non-hazy FTO is the
383 usual FTO layer deposited on a glass substrate, while the diffuse FTO was fabricated by
384 depositing oxide nanoparticles before FTO deposition^[59,95]. The required haze factor values
385 depend drastically upon the desired application. For displays or window defrosting, low haze
386 values are mandatory. For other applications, however, this is less stringent. Although it is an
387 important characteristic, TH haziness is not often reported, preventing the complete
388 benchmarking of TH technologies. **In the case of AgNW networks, the haze factor is directly**
389 **proportional to the areal mass density (usually expressed in mg m^{-2}).^[64] Moreover, it has been**

390 reported that decreasing the diameter or extending the length of AgNWs leads to lower haze
 391 factors.^[96,97]



392

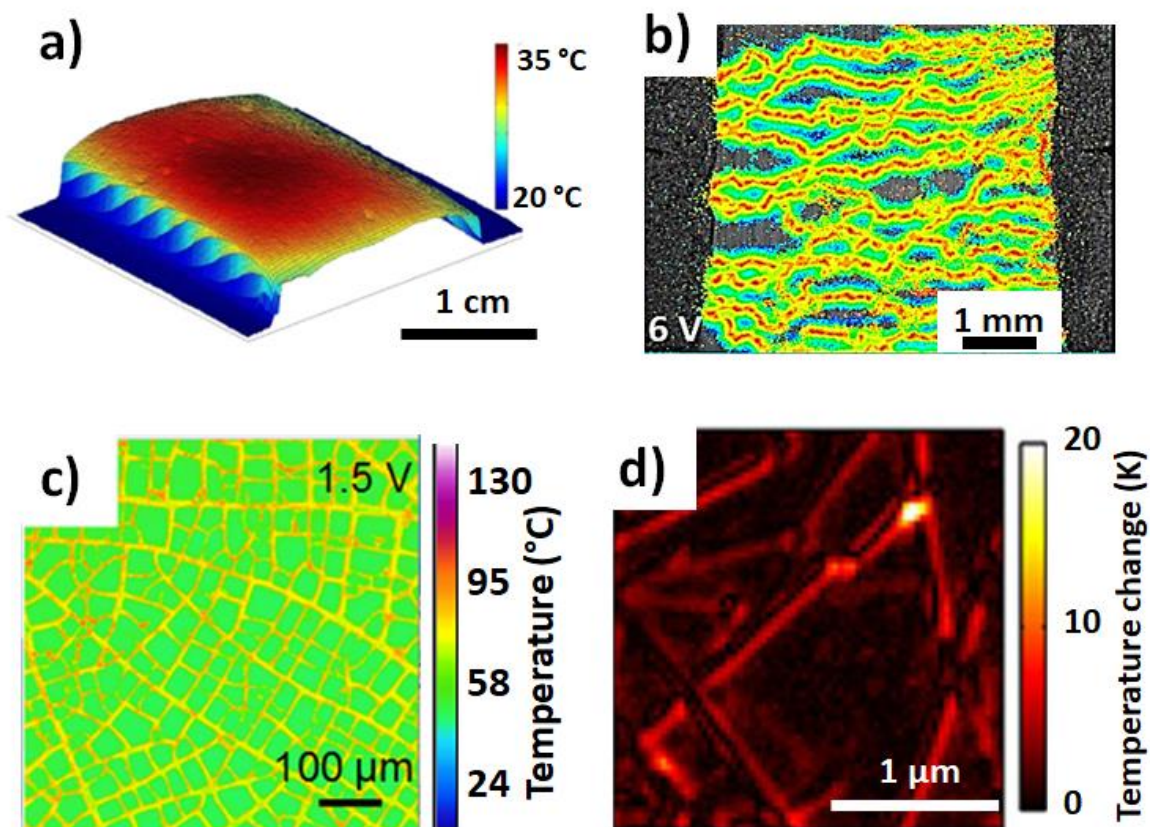
393 **Figure 2.** Optical transmittance of transparent heaters (TH). a) Total and diffuse transmittance, shown
 394 respectively in continuous and dashed lines, for an AgNW network and an FTO layer deposited on bare
 395 optical glass. Both layers have a sheet resistance close to 20 Ω /sq. Metallic nanowire networks are
 396 transparent in the NIR region. b) Schematic representation of the spectrophotometer with the integrating
 397 sphere. Total (diffuse) transmittance is measured with (without) the white plate to include (exclude)
 398 the specular transmittance. c) Pictures of non-hazy (left) and hazy (right) FTO layers on 25x25 mm² glass
 399 substrates.

400

401 **Temperature measurement.** The accurate measurement of temperature is essential for the fine
 402 characterization of THs. Measurements of the temperature produced by THs as a function of
 403 the input voltage or other tuned parameters is expected with high temporal and spatial
 404 resolutions. One can calculate and/or define other characteristic properties that were discussed
 405 in the previous section 2.1, such as steady-state temperature, heating rate, operating voltage,
 406 heat power density, thermal resistance or conductivity, heat transfer coefficient, etc. A common
 407 choice for measuring the temperature is the use of a thermocouple, directly connected to the
 408 studied sample or device. Thermocouples are cheap and cover a wide range of temperatures.
 409 There are several suitable types of thermocouples depending on applications and the
 410 temperature ranges.^[98] The most reported thermocouple in the case of THs is the type K

411 thermocouple. Another way to measure the temperature by direct contact is the use of resistance
412 temperature detectors (RTD) which are based on the increasing electrical resistance of
413 conductors with increasing temperatures. The platinum RTD in particular displays a superior
414 stability and excellent repeatability, but is more expensive than common thermocouples, and
415 has a narrower range of temperature measurement.^[99] Although these types of thermometers
416 are accurate and easy to use, some studies on THs require a precise mapping of the temperature
417 distribution that cannot be performed properly with the sensors described above. Thermal
418 imaging IR cameras detecting radiations in the mid or long-IR range of the electromagnetic
419 spectrum are appropriate. They have become an indispensable experimental tool for specific
420 temperature measurements. The spatial distribution of temperature is an important advantage
421 of IR imaging since it allows the investigation of heating homogeneity, reveals defects that are
422 optically invisible, and moreover it provides the temperature distribution globally in a device
423 and its environment. Radiative temperature measuring is a non-contact method that can be much
424 more convenient when it is hard or impossible to contact with the studied TH. However, IR
425 imaging gives access only to the surface temperature, which is a clear disadvantage, but this
426 does not appear to be a problem for THs since the active films are very thin. Some key
427 parameters for an IR camera are the temperature range and the thermal sensitivity, the spatial
428 resolution and the frame rate. The pixel pitch of these cameras has decreased to 10 microns,
429 and recent studies suggest that it can be lowered down to 5 microns.^[100] Other critical issues of
430 IR imaging are emissivity and reflection. In modern IR cameras these parameters can generally
431 be set by the operator. Almost all of the reported studies for THs use IR imaging. Emissivity is
432 rarely investigated experimentally^[101,102]; that being said, Kim et al. showed that for AgNW-
433 carbon hybrid THs, the emissivity of the tested film heater decreased linearly with the AgNW
434 content^[102]. This information is useful for the quantitative assessment of thermal losses. Finally,
435 another method with higher sensitivity and a submicron spatial resolution is thermoreflectance
436 (TR). It detects temperature changes near the surface using the relationship between optical

437 reflectance and temperature.^[103] It is used for very specific temperature studies, and not to
438 record the temperature in large areas since it is difficult to define an accurate absolute
439 temperature., In the case of AgNW networks for example, TR imaging can record hotspots of
440 individual nanowire junctions in the 300x300 nanometer region size.^[91] In another case a
441 picosecond TR technique was used to study the thermal diffusivity of 30 to 70 nm thick ITO
442 thin films.^[104] **Figure 3** presents examples of IR and TR imaging with the corresponding size
443 scales. Figure 3a represents the temperature profile of AgNW-rGO (reduced graphene oxide),
444 measured by an IR camera with a low pixel resolution of 250 μm x 250 μm . This roughly
445 corresponds to an area with more than one hundred nanowires.^[54] A comparable technique used
446 to reveal defects in microelectronic devices is lock-in thermography (LiT).^[105] It can provide
447 an IR emission intensity and a heat timing map^[106] but does not include any thermal calibration
448 or numerical scale. However, as shown in Figure 3b, it appears very useful to visualize the
449 electrical and thermal distribution in the case of MNW networks. It enables us to investigate
450 the activation of efficient percolating pathways and the detection of hot spots under electrical
451 stress.^[107] In the case of the IR camera shown in Figure 3c, the higher resolution of 1.6 μm
452 helps identify the temperature of each channel of the metal crack template.^[108] Finally,
453 Figure 3d shows how advantageous TR can be to perform temperature studies, for example to
454 image hot spots and nanowire junctions.^[91]



455

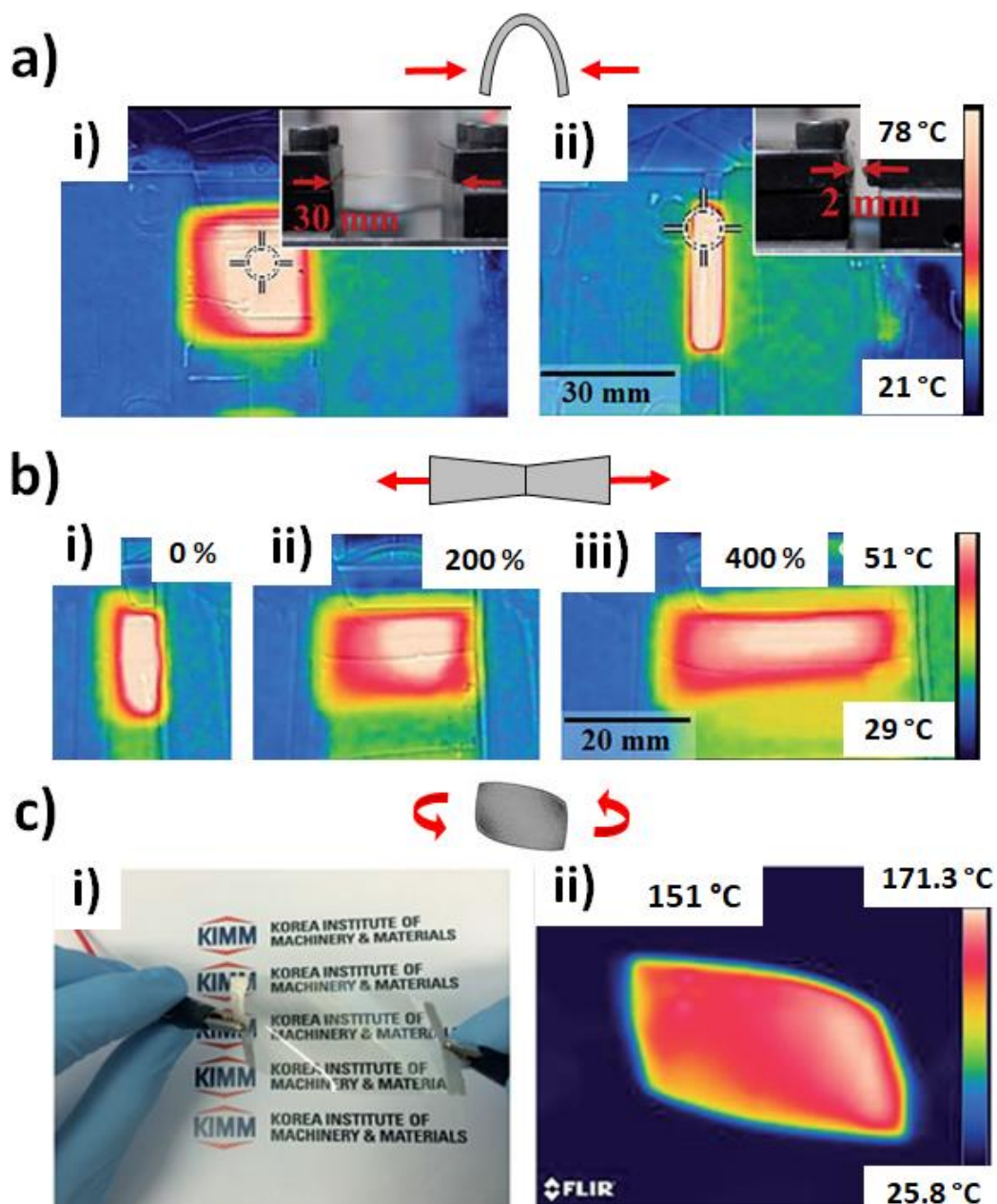
456 **Figure 3.** Thermal imaging methods for characterizing THs at different length scales. a) 3D temperature
 457 profile measured using an IR camera with $250\mu\text{m} \times 250\mu\text{m}$ pixels, for AgNW-rGO after applying an
 458 electrical current of 20 mA for 60 s. Reproduced with permission.^[54] Copyright 2017, IOP Publishing.
 459 b) LiT image of an AgNW network. The efficient percolating pathways can be detected in brighter
 460 colors with a camera of 640×512 pixels resolution with 10 Hz “ON-OFF” voltage cycles of 6V.
 461 Reproduced with permission.^[107] Copyright 2016, American Chemical Society. c) Thermal map of a
 462 metal mesh network fabricated from a crack template under 1.5 V, with IR imaging with $1.6 \mu\text{m}$
 463 resolution. Reproduced with permission.^[108] Copyright 2017, American Chemical Society. d) Enlarged
 464 region of a nanowire network channel, showing representative hotspots using thermoreflectance (TR)
 465 imaging. Reproduced with permission.^[91] Copyright 2015, American Chemical Society.

466 The different types of temperature measurements are carried out and presented as a function of
 467 the electrical properties, since the Joule effect is responsible for the heating. As mentioned
 468 previously, the steady-state temperature (T_{steady}) is an important feature for THs and can be
 469 studied experimentally by applying a constant voltage or areal power density. The time
 470 necessary to reach the steady-state temperature is also measured, and the heating rate is usually
 471 calculated and reported with the corresponding value of the applied voltage. Plotting T_{steady}
 472 versus the input power density values shows a linear relationship, with the slope coefficient
 473 representing the thermal resistance per unit of area. Another typical experiment related to

474 performance measurements of THs is the cyclability or “ON-OFF” test, which consists of
475 switching between the on and off states of the applied bias for a large number of operating
476 cycles.^[102,109]

477 **Mechanical properties.** The first application of THs was during World War II, with the use of
478 stiff tin oxide to defrost the cockpit windshields of aircrafts to allow them to fly at higher
479 altitudes.^[2] These past years, the development of nanotechnology and advances in flexible
480 electronics have given rise to a huge variety of applications that require excellent stability under
481 mechanical stresses (flexibility and even stretchability). As explained hereinafter, TCOs cannot
482 be integrated into very flexible devices, despite their excellent electrical and optical properties.
483 The high temperature deposition process makes it rather impossible to use flexible and
484 transparent polymers as substrates, because these do not have high thermal resistance.^[110] When
485 they are deposited on flexible substrates, the electrical performance of TCOs is often limited
486 due to deformations that appear on these thin films. On the other hand, the flexibility of
487 emerging materials such as CNTs, metallic grids, MNWs and conductive polymers is one of
488 the main reasons why their study is constantly increasing. The measurement of electrical
489 resistance over thousands of bending cycles is a standard experiment reported in the literature.
490 In general, the bending radius (usually of several mm) is provided. This value is important since
491 it indicates to what extent the TH can be bent, sometimes crumpled. For THs, electrical
492 conductivity must not be altered by mechanical stresses, and the thermal performance should
493 remain stable. In order to estimate the mechanical behavior of THs, the temperature is usually
494 monitored simultaneously to bending. IR imaging, as a contactless method, is particularly
495 convenient for the direct evaluation of performances. **Figure 4a** presents typical examples of
496 bending tests while Figure 4b exhibits stretching tests with concomitant temperature recording
497 by IR camera. Twisting tests, as shown in Figure 4c, are also sometimes reported, depending
498 on the specific application needs. High flexibility has become a common target for emerging

499 TCMs. Interest has also recently been focused on stretchability, which is intrinsically more
500 complicated. The loss of electrical conductivity can be either total, low or negligible depending
501 on several parameters such as the amount of conductive material or the choice of material itself.
502 Ongoing investigations on stretchable THs with an association of different materials (leading
503 to nanocomposites or hybrid materials, see section 3.5) lead to promising features.^[22,70,111]
504 Finally, the incorporation of TCMs into elastic substrates, and the adhesion to various types of
505 substrates is another issue concerning mechanical properties which could influence the
506 performance of TH applications. **Embedded structures can be a promising strategy to tackle**
507 **adhesion issues.**^[81] Measuring performance stability after repeating tape tests^[47,112,113] and
508 microscopic observations of the adhesion between the layers are useful techniques to determine
509 the key drivers that should be studied in depth.



510

511 **Figure 4.** Infrared observations of THs when submitted to different mechanical stress modes. a)
 512 Photographs and IR images of an AgNW film during bending tests at i) the initial conformation and ii)
 513 the final conformation. The AgNW film ($R_{sh}=15 \Omega/\text{sq}$, $Tr=95\%$) was supplied with a voltage of 5 V.
 514 b) During the stretching experiment at: i) the initial state ($L=10 \text{ mm}$), ii) the intermediate stages of
 515 stretching with the strain values in percentage shown in the insets, and iii) the final state ($L=50 \text{ mm}$).
 516 The substrate was a stretchable eco-flex. a,b) Reproduced with permission.^[114] Copyright 2017, Royal
 517 Society of Chemistry. c) Mechanical flexibility and stability of a CuNi TH on a polymer substrate: i)
 518 picture and ii) IR image of the heater at 9 V bias under twisting conditions. Reproduced with
 519 permission.^[115] Copyright 2017, Royal Society of Chemistry.

520

521 **Stability.** Electrical, thermal, mechanical and chemical stabilities are key parameters for TH
 522 performance. Firstly, it is necessary to verify that electrical conductivity and heat emitted

523 remain stable in the long run when THs undergo electrical stresses. Several tests can be
524 performed, like a voltage ramp and/or plateau cycles with resistance and temperature
525 recordings. The “ON-OFF” test described above is another typical stability experiment that is
526 performed in most TH studies. The application of a constant voltage/power for hours in order
527 to check if the temperature remains stable^[116] is also usually carried out. In other cases,
528 constantly increasing voltage ramps are applied until the breakdown of the heating
529 performance, followed by the application of lower voltages to investigate potential
530 reversibility.^[46] These experiments have proven that the encapsulation of heating materials with
531 protective coatings is an excellent choice to improve stabilization. Thermal stability is crucial
532 for THs and it is linked to the potential degradation of active materials or surrounding materials
533 due to high operating temperatures and fast heating/cooling rates. A way to study this is to
534 measure electrical resistance under thermal stress (thermal ramps or plateaus) without applying
535 any electrical power (except a very small current for the resistance measurement). It is also
536 important to investigate the intrinsic heat stability of the substrates used to fabricate a TH,
537 especially in the case of flexible polymers, which are known to limit the stability of flexible
538 THs. Regarding chemical oxidation and ageing, typical measurements are carried out in
539 environmental chambers and involve the simultaneous exposure to controlled humidity and
540 temperature, combined with light irradiation^[48,117]. Generally, the relative humidity chosen is
541 over 80 %, and the temperature between 45°C and 90°C, which covers most of the harshest use
542 conditions.^[70,93,118–121] Study durations varies strongly, and usually depends on the anticipated
543 stability of the TH and on the expected lifetime of its components. For example, stability studies
544 for copper nanowire (CuNW)/NPs usually last minutes^[120] or hours^[118,119], while for AgNW
545 the duration of the study can be days^[70] or months^[121]. Of note, there are some large
546 discrepancies in terms of MNW network stability from one research group to another, probably
547 originating from differences in MNW growth conditions and purification processes, leading to
548 different surface chemistries, and consequently to more or less stable MNW networks.

549

550 3 The investigated materials technologies for transparent heaters

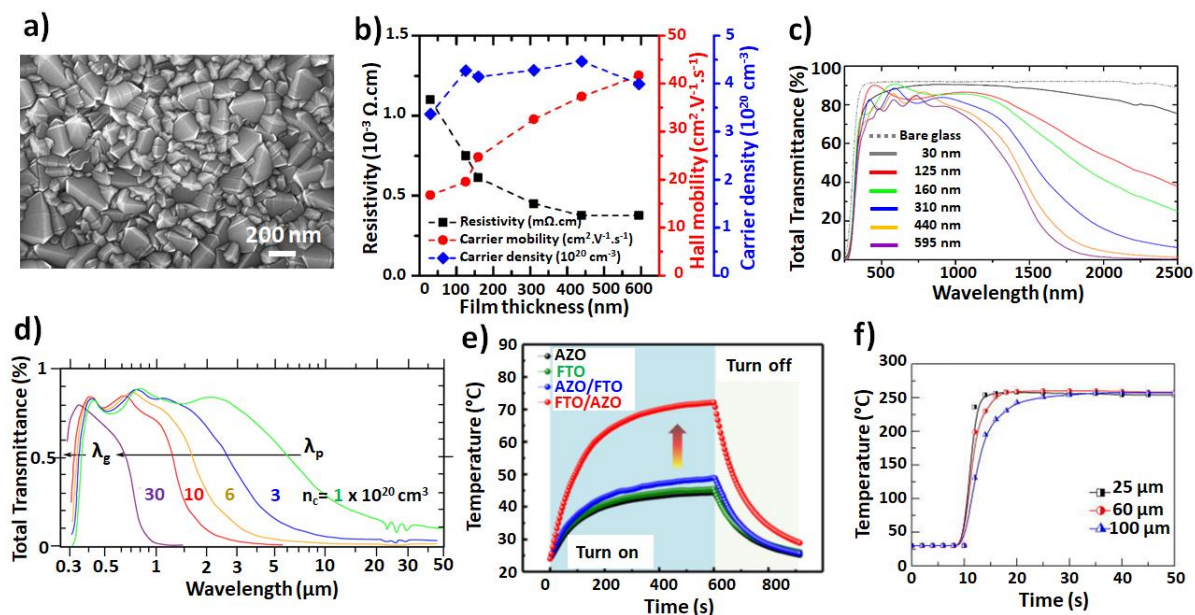
551 Several material technologies for TH applications have been thoroughly investigated. The very
552 first type of thin layers were TCOs, which have been investigated for several decades^[2,9,14,17,59].
553 These thin films of metal oxide have been studied for several applications, including transparent
554 electrodes for solar cells or touch screens, and have already been widely integrated in industrial
555 devices.^[7,10] For THs, like for transparent electrodes, industrial needs have prompted research
556 into other materials^[21]. There are several reasons for this. TCOs, for instance, are ceramic and
557 therefore do not usually withstand any mechanical stress; this makes them incompatible with
558 flexible applications. Moreover, lowering the cost is a strong argument against the vacuum-
559 process and/or the use of indium in the classical indium tin oxide (ITO), due to the scarcity of
560 indium. Likewise, the search for properties that are better adapted to industrial requirements
561 necessitates the exploration of other materials. The goal of this part 3 is to present the main
562 materials categories and their related properties when used for THs. Each type of materials will
563 then be discussed in more detail below, starting with metallic oxide-based materials, then
564 carbon-based nanomaterials (graphene and CNTs), metallic-based materials, conductive
565 polymers and finally nanocomposites or hybrid materials. In this review we consider that
566 *nanocomposites* are materials for which the nanostructures are within a continuous phase such
567 as a matrix, while *hybrid* nanomaterials refer to combination of materials of different natures
568 such as organic-inorganic.

569

570 3.1 Metallic oxide-based materials

571 Among all the different types of TCMs, TCOs were the first to be developed and studied. They
572 have been used industrially for a long time and in many different applications. ITO thin films,
573 in particular, have been employed for the production of THs to defrost aircraft windshields. The
574 basic properties of TCOs have been extensively described in previous works, and we refer the

575 reader to those for additional details^[9,122,123]. Of note, the morphology and structure of TCO
 576 thin films play a key role in their conductivity. These thin films usually exhibit polycrystalline
 577 structures, as shown in **Figure 5a**, with crystal sizes that depend on the deposition method used
 578 and other parameters like film thickness. The latter can easily reach hundreds of nanometers.^[14]
 579 Twins are often observed (for FTO for instance), and as in the case of grain boundaries, they
 580 are detrimental to charge mobility^[14,59,124]. The fact that grains often become bigger as the film
 581 thickness increases has a direct impact on the conductivity of the layers, since the number of
 582 grain boundaries and twins decreases (Figure 5b). Another important aspect of TCOs is the fact
 583 that transparency in the IR region of the spectrum falls rapidly with film thickness or with
 584 carrier concentration due to plasmonic absorption as shown, respectively, in Figure 5c and
 585 5d.^[20] For TH applications where IR transparency is important, e.g. night vision applications
 586 for glasses and binoculars, the TCO technology is therefore not perfectly adapted compared to
 587 other TH technologies.



588

589 **Figure 5.** Transparent conductive oxides (TCO) used as THs. a) SEM image of a typical 400 nm thick
 590 FTO layer showing the grain-boundary structure of the thin polycrystalline film. b) Main electrical
 591 characteristics of FTO layers vs film thickness: electrical resistivity, carrier mobility and carrier density.
 592 Reproduced with permission.^[14] Copyright 2013, AIP Publishing. c) Total optical transmittance for
 593 different FTO film thicknesses: the thicker the film, the lower the transmittance, specifically in the near
 594 infra-red region due to plasmonic absorption. d) Computed spectral normal transmittance of ITO. The
 595 values correspond to electron density. Reproduced with permission.^[125] Copyright 1986, AIP

596 Publishing. e) Time dependence of temperature when a 12 V voltage is applied to a TH composed of
597 either an AZO layer (black), a single FTO layer (green), an AZO/FTO (blue) or a FTO/AZO (red)
598 double-layer film on glass which shows different electrical properties. This clearly illustrates the strong
599 influence of the TH electrical properties on the heating performance. Reproduced with permission.^[84]
600 Copyright 2014 John Wiley and Sons. f) Measured temperature vs time for a 100 nm-thick AZO-based
601 TH, deposited on mica substrates of different thicknesses, illustrating the role played by the thermal
602 inertia of the substrate in terms of response time. Reproduced with permission.^[60] Copyright 2018,
603 AIP Publishing.

604
605 Despite TCOs being the oldest studied TCMs, there are surprisingly few reports in the literature
606 dealing with the application of TCOs as THs. The studies reported so far involve ZnO-based
607 materials, Ga-doped ZnO (GZO)^[126–128] and Al-doped ZnO (AZO)^[60,84,127,129], FTO^[84] and
608 ITO^[130–133]. Indeed, TCOs have been mainly investigated in the framework of industrial
609 research and development, which is generally not associated with scientific publications.

610 In industry, ITO is routinely deposited by sputtering, a vacuum method that is generally
611 associated with higher costs compared with solution process technologies. Im et al. explored
612 the utilization of ITO nanoparticle (NP) solutions to process ITO thin films^[130] as an alternative
613 to vacuum processing. The films were fabricated by spin-coating the ITO NP solution on a glass
614 substrate, followed by annealing up to 400 °C. The main effect of the annealing step is to sinter
615 the particles. Using these films, a temperature of 163 °C was achieved for a bias voltage of 20
616 V, and dry-ice was used to demonstrate the defrosting capabilities of the TH.^[130] More recently,
617 Kim et al. used the same approach. However, by increasing the annealing temperature of the
618 deposited ITO NP and by using different atmospheres during the annealing step, they
619 demonstrated that the oxygen vacancies in the film can be controlled^[131]. In this case,
620 temperatures up to 215 °C were reached for a 15V bias, with a thermal efficiency of 162.9
621 °C/(W/cm²) being obtained for optimized samples. In another study, Yang et al. demonstrated
622 that by adding organic additives such as polymethyl methacrylate and terpineol to the ITO NP
623 solution, the obtained heaters are more efficient and homogeneous. The authors made micro-
624 heaters using this approach, and could reach temperatures of 445 °C for a bias voltage of only
625 12 V.^[132]

626 Kim et al. explored the use of bilayers by combining AZO and FTO deposited by sputtering
627 and Chemical Vapor Deposition (CVD), respectively.^[84] They observed that both conductivity
628 and transparency improved for bilayers with respect to single layers of the same thickness, as
629 demonstrated in Figure 5e.^[84] This is attributed to the higher overall particle size in the film,
630 which affects both mobility and transparency. The best results, reported in Figure 5e, were
631 obtained for FTO/AZO bilayers for which temperatures above 70°C were obtained for a bias
632 voltage of 12 V.^[84] Roul et al. studied rigid and flexible AZO-based TCOs by depositing AZO
633 on glass and polyethylene terephthalate (PET) substrates by magnetron sputtering.^[129] The
634 films deposited on glass reached temperatures of approximately 100°C for a 12 V bias for the
635 samples deposited at 200 °C. Flexible heaters made on PET reached 50°C for bias voltages of
636 8 V. Nevertheless, stability results are only shown for AZO/glass samples, and no study of the
637 effect of bending on the properties of the flexible TH is reported. It is also worth mentioning
638 that ZnO-based TCOs may not be the best candidates for high temperature applications, since
639 ZnO tends to absorb oxygen species in the grain boundaries, which has a detrimental effect on
640 mobility, as explained and modelled recently.^[19] It has been shown that the absorption of
641 oxygen species increases rapidly with temperature^[134], thus most likely limiting the applications
642 of THs based on AZO.

643 Ke et al. showed that despite the ceramic nature of ITO, flexible THs can be obtained by using
644 mica substrates as thin as 15 µm, thanks to their layered structure.^[133] ITO layers of up to 500
645 nm were deposited by pulsed laser deposition (PLD) at room temperature and annealed at up to
646 500°C. Flexible THs were fabricated, exhibiting fast ramping. Temperatures of up to 438°C
647 were reached in less than 15 s at a bias voltage of 19 V. The same approach was used by the
648 same authors to make flexible THs based on AZO/mica.^[60] Figure 5f shows the measured
649 temperature versus time for a 100 nm-thick AZO-based TH deposited on mica substrates of
650 different thicknesses: this illustrates the role played by the thermal inertia of the substrate,^[60] in
651 agreement with equation (4). Record heating rates of 200°C/s were obtained in this case. The

652 occurrence of van der Waals epitaxy between the mica substrate and the grown AZO film
653 reasonably explained this superior performance.

654 Gallium has also traditionally been used to dope ZnO. Jayathilake et al. deposited ZnO co-
655 doped with Al and Ga (AGZO) by aerosol-assisted chemical transport, which showed a lower
656 conductivity than AZO or GZO films^[127]. The films were prepared by dispersing previously
657 prepared AGZO powders (by microwave synthesis) in a methanol solution containing formic
658 acid and cellulose. Then aerosol generated from this suspension was carried by N₂ gas to a glass
659 substrate at 400 °C. Temperatures above 132 °C were achieved in 10 min for bias voltages of
660 18 V. Older reports on physically deposited GZO films were performed by Kim et al.^[128] and
661 Ahn et al.^[126] In the first case, the films were deposited by rf-magnetron sputtering on glass
662 substrates^[128] and reached 90 °C after 22 s for a bias voltage of 48 V. In the second case, PLD
663 was used to deposit the films on glass substrates, and reached over 88 °C after 48 s for a 12 V
664 bias.^[126]

665 Thus, while TCOs, and in particular ITO, are the most prominent transparent materials today,
666 with a broad range of industrial applications, fundamental studies involving promising
667 approaches are still being carried out in order to push the limits of these materials in terms of
668 performance and mechanical flexibility. These studies are framed in a wider research that
669 involves the exploration of competing materials, such as carbon-based nanomaterials, which
670 are described in the next section.

671

672 **3.2 Carbon-based nanomaterials (CNTs & graphene)**

673 Carbon-based thin film heaters were first described in 2007.^[27] Carbon fibers, carbon nanotubes
674 (CNTs) or graphene derivatives have been widely reported in the literature to address several
675 fields of applications including defogging,^[135] anti-icing, de-icing,^[83,136,137] wearable
676 electronics,^[138,139] thermochromic displays^[140,141] or thermomechanical sensors.^[62]

677 Most published studies report the use of carbon-based thin film heaters for the assessment of
678 non-transparent devices. Their high flexibility and stretchability are, without doubt, advantages
679 that make them very interesting for various type of heaters thanks to their remarkable
680 mechanical properties, while conversely they exhibit low transparency.^[57] Since this review
681 focuses on THs, only devices or active materials with good transparency are discussed
682 hereinafter.

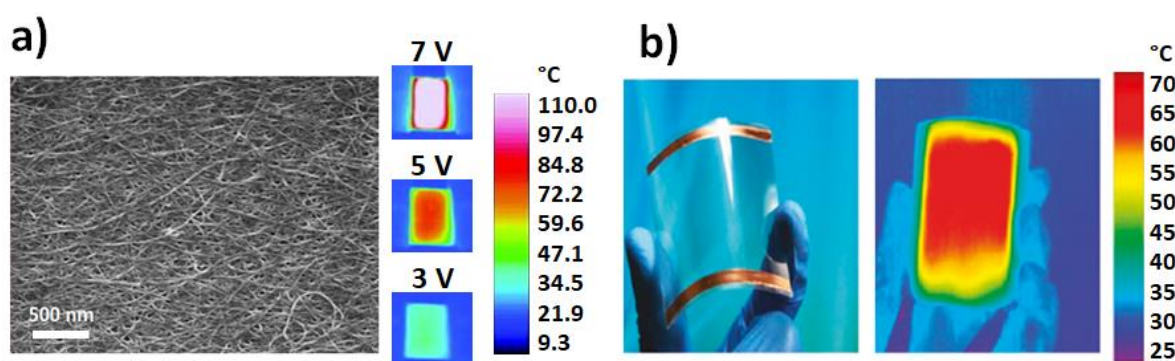
683 Active parts of carbon-based THs can be processed either by dry or solution-based routes, the
684 latter being often more suitable for many supports (PEN, PET, PC, PI or cotton fabrics for
685 example). CNT devices can be produced either through percolative networks implying printing
686 processes^[61], or thanks to CNT forest (aligned CNTs, usually prepared by chemical vapor
687 deposition (CVD) / transfer protocol). For the first method, **Figure 6a** shows an SEM image of
688 a transparent and flexible single wall carbon nanotubes (SWCNT) heater prepared on a plastic
689 substrate, along the associated IR images at various applied voltages.^[61] Regarding graphene
690 and its derivatives, exfoliation of graphite or chemical reduction of GO were reported. Recently,
691 unusual and interesting approaches based on the use of carbon nanosheets from the
692 carbonization of polymers or from natural carbonaceous by-products of ethylene production
693 were published by Souri et al. ^[142] and by Morris et al.^[143], respectively.

694 Both the deposition processes and the intrinsic properties of the material strongly impact the
695 performances of carbon-based THs. For CNT networks, the trade-off between transparency and
696 conductivity can also be controlled by nanotube types (e.g. single-walled vs multi-walled
697 MWCNT). SWCNTs generally exhibit high transparency and low haze, but rather low
698 conductivity due to the presence of poorly conductive semi-conducting CNTs and resistive
699 CNT-CNT junctions.^[61,144] MWCNT-based electrodes (100% of metallic behavior tubes) are
700 more conductive but less transparent due to their larger size, and exhibit a higher haze value.^[145]
701 Figure 6b exhibits optical and infrared pictures of graphene-based THs illustrating both
702 flexibility and uniformity.^[57] In the case of percolative networks of graphene flakes, each

703 graphene layer decreases the transparency by $\sim 2\text{-}3\%$. However, devices made of a graphene
 704 monolayer obtained by dry deposition keep a very high level of transparency, but this technique
 705 is somewhat limited to small surfaces. Improvement is still required in terms of uniformity of
 706 highly conductive graphene layers and larger surface coverage. Due to the higher electrical
 707 contact resistances between the conductive objects of carbon-based networks (CNTs, Carbon
 708 flakes) compared to MNW networks, most carbon-based THs require denser systems to reach
 709 the same level of conductivity, at the expense of the transparency.

710 As input voltage and surface temperature are strongly correlated to sheet resistance, in most
 711 cases, carbon-based THs are addressed with high input voltages from 10 to 100V for at most a
 712 few cm^2 samples. Indeed, transmittances higher than 70% are achievable at several hundreds of
 713 Ω/sq .^[146] On polyimide substrates, temperatures higher than 350°C have been reached.^[142]
 714 Considering that surface power densities of a few kW/m^2 are required for both thermal comfort
 715 and heating, the lifetime and stability of carbon-based materials are a true asset of carbon-based
 716 THs.

717 In the case of carbon-based THs, transparency is clearly impaired if one intends to reach low
 718 sheet resistance for high heating performance. New developments using carbon nanostructures
 719 hybridized with metallic nanowires could provide an interesting alternative since carbon-based
 720 materials can significantly enhance the stability of metallic nanowires (See section 3.5.1).



721
 722 **Figure 6.** Performances of carbon-based transparent heaters on flexible substrates. a) SEM pictures and
 723 infrared pictures of SWCNT-based transparent electrodes when submitted to applied voltages of 3, 5 or
 724 7 volts. Reproduced with permission.^[61] Copyright 2017, AIP Publishing b) Highly flexible graphene-

725 based TH with optical and infrared pictures illustrating both flexibility and uniformity. Reproduced with
726 permission.^[57] Copyright 2011, American Chemical Society.

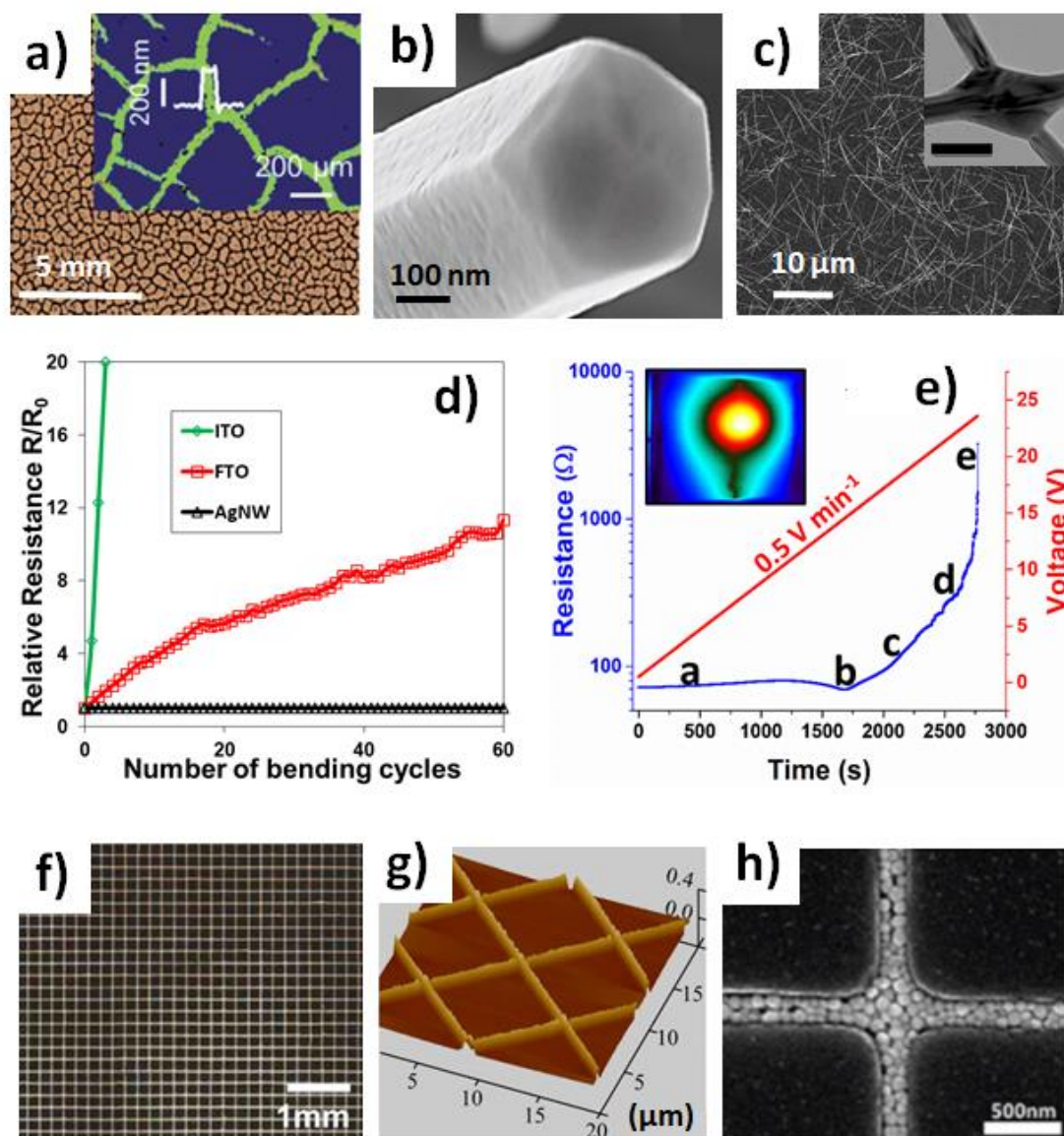
727

728 **3.3 Metallic-based materials: metallic grids, metallic meshes, MNW random networks**

729 While TCOs have been largely studied for several decades to be used as transparent electrodes
730 (TEs) or THs, other materials such as metallic-based nanostructures have been considered since
731 the year 2000 approximately^[21,147]. They present additional properties when compared with
732 TCOs, since many of them can be deposited at low temperatures and exhibit good mechanical
733 flexibility. Metals indeed appear attractive as potential TH active materials since they possess
734 very high electrical and thermal conductivities. For instance, silver exhibits the highest
735 conductivities among all materials at room temperature. However, ultrathin metallic films
736 generally do not show an interesting trade-off between optical transparency and sheet
737 resistance, due to both strong light absorption and electron scattering at surfaces or interfaces.
738 As such, the only way to take advantage of metals for TH applications is to engineer metal
739 nanostructures. This can provide interesting opportunities to manipulate photons and electrons
740 in order to achieve electrical, optical and mechanical properties that are not reachable with
741 TCOs. The main metallic patterns that can be efficiently used for TH production are metallic
742 meshes, MNW networks and metallic grids. The difference between metallic grids and meshes
743 in the literature is sometimes confusing. In this review we will consider that *metallic meshes* do
744 not contain privileged directions in terms of conductive lines, while *metallic grids* are
745 constituted by a periodic arrangement of metal lines, generally with a 3- or 4-fold symmetry.
746 In this section, we will briefly examine the different investigated metallic-based materials, by
747 describing their main features, properties and their potential integration into TH devices.
748 Progresses toward low-cost TH fabrication, wire-wire junction resistance, physical properties,
749 adhesion and stability will also briefly be discussed.

750 Metallic meshes can exhibit some interesting features as THs. As shown by Kiruthika et al.
751 interconnected crackles can be obtained thanks to the spreading of low cost crackle wall paint

752 by using the drop coating technique.^[82] Interconnected Ag meshes can be fabricated by
753 depositing a thin metal layer on top of the obtained crackles and then removing the template.
754 **Figure 7a** shows a typical optical image of an Ag mesh fabricated on glass, while the inset
755 corresponds to the optical profiler image (the thickness is approximately 300 nm).^[82] This type
756 of metallic mesh network exhibits interesting physical properties on large areas. Kiruthika et
757 al. reported a sheet resistance of 1 Ω /sq on an 18x15 cm² area, associated to an optical
758 transmittance of 77%.^[82] Thanks to the low electrical resistance, the use of metallic meshes as
759 THs requires a rather low voltage: an 8.5 V bias was used to reach uniformly heated surfaces
760 of up to 170°C. This efficient defrosting device successfully withstood an ultra-sonication test,
761 as well as many defrosting cycles.^[82] Metallic mesh networks have been the subject of many
762 studies lately, with various metallic species being evaluated, like copper,^[148] silver,^[149,150]
763 nickel,^[151] cupronickel,^[115] gold^[152] and platinum.^[72]



764

765 **Figure 7.** Main features of metallic-based THs. a) Optical image of an Ag mesh fabricated on glass; the
 766 inset corresponds to the optical profiler image (thickness of about 300 nm). Reproduced with permission.
 767 ^[82] Copyright 2014, Royal Society of Chemistry. b) High-resolution SEM image of a copper nanowire
 768 (CuNW) with a 5-fold symmetry. Reproduced with permission.^[66] Copyright 2017, John Wiley and
 769 Sons. c) Typical SEM picture of an AgNW random network. The inset shows a TEM picture of a sintered
 770 junction between two nanowires (bar scale: 100 nm).^[153] d) Relative electrical resistance of different
 771 types of TH materials (ITO, FTO and AgNW) versus the number of bending cycles at 5 mm radius of
 772 curvature. Reproduced with permission.^[20] Copyright 2016, John Wiley and Sons. e) Evolution of the
 773 electrical resistance of an AgNW network during a voltage ramp of 0.5 V/min. The electrical resistance
 774 exhibits a drastic increase associated to the appearance and propagation of a crack, as revealed by the
 775 IR image in the inset (the width of the IR image corresponds to 25 mm). Reproduced with permission.^[93]
 776 Copyright 2018, American Chemical Society. f) Optical microscopy image of a flexible transparent Au
 777 grid electrode with the following geometrical features: grid width: 4.5 μm; grid spacing: 200 μm; Au
 778 thickness: ~90 nm. Reproduced with permission.^[154] Copyright 2014, American Chemical Society. g)
 779 AFM profile sections of a silver grid fabricated by femtosecond laser writing of a silver aqueous
 780 solution. The profile shows a good uniformity of the grid. Reproduced with permission.^[155] Copyright
 781 2016, AIP Publishing. h) SEM image of the silver nanoparticle (AgNP)-based metallic grid fabricated
 782 by capillary assembly of AgNPs. Reproduced with permission.^[156] Copyright 2016, Royal Society of
 783 Chemistry.

784

785 MNW networks have been the subject of a lot of research lately, with a focus on the industrial
786 integration of the networks as transparent electrodes into opto-electronic devices, as recently
787 reviewed by several authors.^[20,38,39,157,158] Among the possible MNW materials, silver has been

788 the most investigated^[33,34,39,159–162], while CuNW networks constitute an interesting
789 alternative.^[48,66,76,163,164] Figure 7b exhibits a high-resolution TEM image of a CuNW showing
790 the 5-fold symmetry.^[66] Figure 7c reports a typical SEM picture of a random AgNW network.

791 The inset shows a TEM picture of a well-sintered junction between two AgNWs,^[153] knowing
792 that an efficient local sintering of the junction between the different AgNWs leads to lower
793 junction's electrical resistance and, therefore, to lower overall network electrical resistance.^[90]

794 While the most used deposition techniques are spin-coating and spray-coating, several original
795 methods have been proposed lately to fabricate AgNW networks with good performances. For
796 instance, Hu et al. proposed a versatile agitation-assisted assembly approach that induces an
797 orientation of AgNWs. This leads to excellent performances with a R_{sh} value of 2.8 Ω/sq , an
798 optical transparency of 85% and a high stretchability of up to 40%.^[68] The electrical resistance
799 of junctions between AgNWs can be reduced by several methods, such as thermal annealing,^[90]
800 UV treatment^[165] or as shown recently by Huang et al. using a self-limited nano-soldering

801 method. This method can decrease R_{sh} from 18.6 to 7.7 Ω/sq while preserving a constant optical
802 transmittance of 90%.^[166] The first demonstration of AgNW networks being efficiently used as
803 THs was published in 2012 by Celle et al..^[42] These authors showed that the intrinsic features

804 of AgNW random networks made it possible to combine bendability, transparency and high
805 heating performances at low voltages (below 12 V), which constitutes a clear asset for
806 integration in many applications.^[42] This demonstration, on both glass and polymeric
807 substrates, was followed by numerous publications. Sorel et al..^[43] published in 2014 a

808 comprehensive physical approach of AgNW network-based THs, including the different

809 regimes associated with low network density (percolative regime) and high network density
810 (bulk-like regime). The authors also provided critical considerations related to electrical
811 conductivity, optical transparency and heat dissipation for efficient THs. Figure 7d shows the
812 relative electrical resistance of different types of TH technologies (ITO, FTO and AgNW)
813 versus the number of bending cycles with a radius of curvature of 5 mm. AgNW networks are
814 much more flexible than TCOs.^[20] However, one of the main issues with MNW networks is
815 their relative low stability under electrical and/or thermal stresses, even at device-operating
816 conditions, as reported in several studies.^[46,54,90,167,168] This is illustrated in Figure 7e, which
817 displays the evolution of the electrical resistance of an AgNW network during a voltage ramp
818 of 0.5 V/min. The electrical resistance exhibits a drastic increase associated to the appearance
819 and propagation of a crack, as revealed by the IR image in the inset (the width of the IR image
820 corresponds to 25 mm).^[93] As reported below (section 3.5.3), the deposition of a thin oxide
821 layer on top of MNW networks drastically enhances their stability or their adhesion.^[47,48,167]
822 These nanocomposites can lead to efficient and stable THs,^[44,46,47,117,169] as discussed further in
823 section 3.5.

824 Metallic grids have been the subject of a lot of research since they appeared as promising
825 transparent electrodes, with both optical transmittance and sheet resistance being well
826 controlled by adjusting the period and width/thickness of the patterns.^[147,170] The metal lines
827 are thin enough (~few μm) to provide a low sheet resistance, while the period of the grid is
828 large enough (~5-200 μm) to provide sufficient transparency but not too large, to ensure heating
829 uniformity over the entire TH. Figure 7f shows a typical optical image of a flexible transparent
830 Au grid electrode with the following geometrical features: grid width of 4.5 μm , grid spacing
831 of 200 μm , Au thickness of ~90 nm.^[154] This Au grid electrode exhibits an optical transmittance
832 of 92% at 550 nm and a sheet resistance of 97 Ω/sq .^[154] The fabrication of metal mesh electrodes
833 was originally performed using vapor deposition processes, which require vacuum and generate
834 metal waste. Consequently, many studies have investigated other reliable fabrication methods,

835 and in particular large area printing methods like flexography, slot-casting, screen printing and
836 others. Figure 7g exhibits an AFM profile section of a silver grid, fabricated by femtosecond
837 laser writing of a silver aqueous solution, which shows the good uniformity of the grid.^[155] This
838 fabrication method possesses advantages in terms of flexibility and adaptability compared to
839 alternative techniques like the combination of metal evaporation and lithography. Figure 7h
840 shows an SEM image of a silver nanoparticle-based (AgNP) metallic grid fabricated by
841 capillary assembly of AgNP.^[156] Of note, metallic grids can exhibit excellent flexibility.^[147]
842 However, one of the potential weaknesses of metal grids is the weak adhesion to the substrate.
843 Lee et al proposed to enhance this adhesion through colloidal deposition and silver
844 enhancement steps. This improves the adhesion of the metal mesh thanks to an intermediate
845 adhesion layer based on 3-aminopropyltriethoxysilane.^[112] This approach results in an optical
846 transmittance of 97.7% and a sheet resistance of 71.6 Ω /sq, and its use as a TH enables to
847 homogeneously reach a temperature of 245°C under an applied voltage of 7 V, showing a clear
848 enhancement of adhesion.^[112] Another very promising strategy to tackle adhesion issues relies
849 on embedded structures since they can: i/ enhance the surface smoothness, ii/ improve
850 drastically the mechanical stability and iii/ induce strong adhesion to the substrate. Khan et al.
851 demonstrated a cost-effective electrodeposition solution process of embedded metal-mesh with
852 excellent mechanical, optical and heating performances.^[74] Of note, metallic fibers (with
853 diameters much larger than nanowires) can exhibit interesting properties. Wang et al. recently
854 demonstrated that percolating networks of Ag nanofibers fabricated by blow-spinning
855 constitute efficient THs.^[73] This TH technology can indeed exhibit good optical and electrical
856 properties, as demonstrated with Ag nanofibers networks that were obtained with an optical
857 transmittance of 95% and a sheet resistance of 16 Ω /sq, enabling to reach temperatures larger
858 than 285°C with a 10 V bias.^[73] Singh et al. reported a TH with low operating voltage based on
859 embedded PVA@Ag nanofiber network. This TCM structure has a smooth surface topology
860 and excellent bending stability after 10 000 bending cycles at 1.0 mm bending radius.^[81] In the

861 case of copper based fibers, Jo et al. demonstrated a highly stretchable and transparent TH with
862 ultra-low sheet resistance that can keep the working temperature constant up to 300 %
863 stretching.^[76]

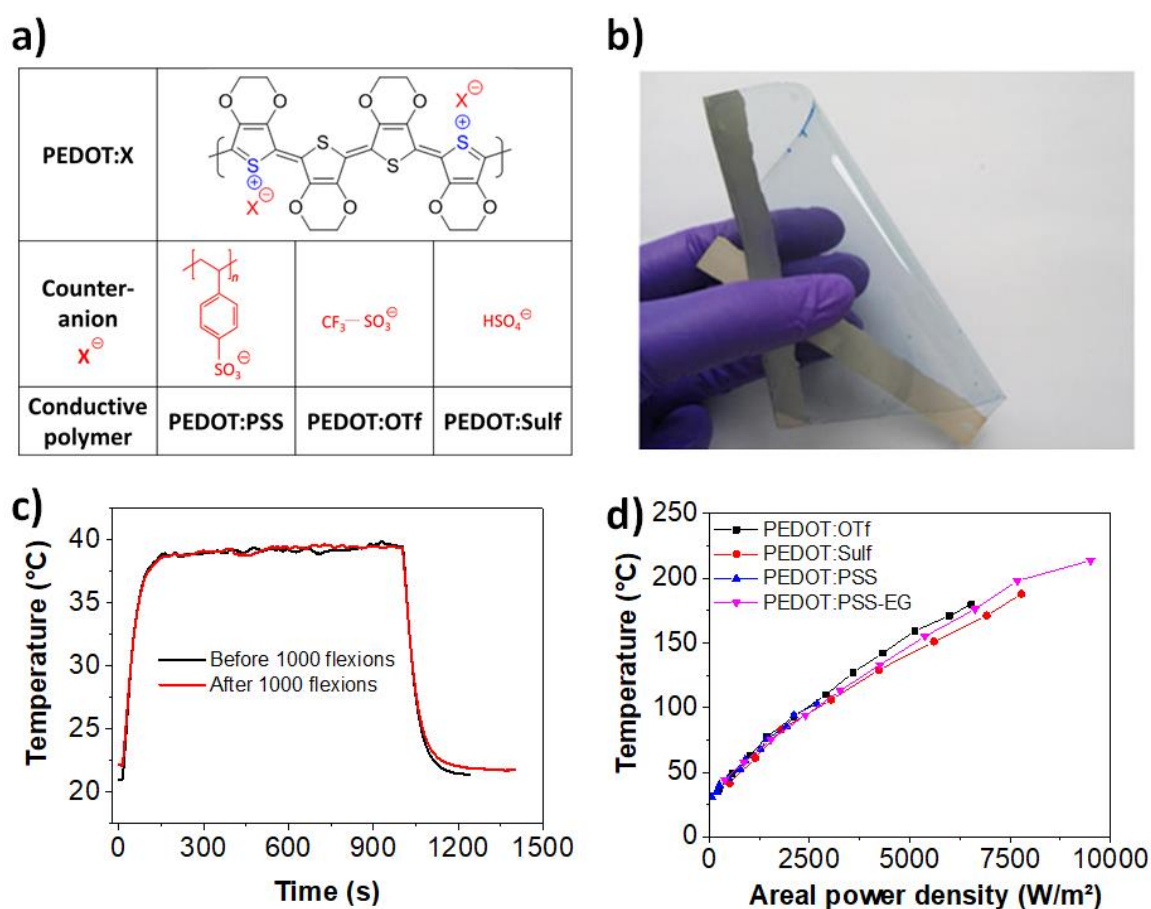
864

865 **3.4 Polymer-based materials**

866 Conductive polymers present attractive features for TH fabrication in terms of
867 flexibility/stretchability, cost and processability. However, only few of them exhibit an
868 electrical conductivity suitable for TH applications.

869 Recently, a breakthrough was performed in TH fabrication with the first demonstration of a
870 100% polymeric TH. Gueye et al. demonstrated the ability of poly(3,4-ethylenedioxythiophene)
871 (PEDOT)-based thin films to be efficient THs, without the need for metal or conductive
872 fillers.^[50] Three conductive polymers were studied (i) PEDOT doped with polystyrene sulfonate
873 (PSS) and with ethylene glycol (EG): PEDOT:PSS-EG, (ii) PEDOT doped with
874 trifluoromethanesulfonate CF_3SO_3^- (OTf): PEDOT:OTf, and (iii) PEDOT:OTf thin films
875 treated with dilute sulfuric acid to further enhance conductivity: PEDOT:Sulf. The chemical
876 structures are displayed in **Figure 8a**. These conductive polymers show excellent
877 optoelectronic and heating properties^[50], and are flexible, as shown in Figure 8b. The electrical
878 resistance and heating properties of the polymer-based TH remain stable under strong
879 mechanical stress (1000 cycles with a 9 mm bending radius), as shown in Figure 8c.
880 Temperatures higher than 100 °C can be reached in a few minutes with a bias of less than 12 V
881 (Figure 8d). Transparencies higher than 87% are generally obtained with extremely low light
882 diffusion, the haze value being typically under 1%. This aspect is very important because
883 haziness is a critical parameter for most optoelectronic applications, and such low values are
884 hardly ever achieved with other non-TCO materials.^[38] This polymer-based technology made
885 it possible to reach high power densities, up to 10 000 W/m² (Figure 8d). Heating homogeneity,

886 measured by IR imaging, and extended mechanical stability were demonstrated. Chemical
 887 instability could have been anticipated because PEDOT-based materials are known to be
 888 sensitive to light and moisture. However, after encapsulation with a barrier film, a loss of only
 889 1°C was measured after 200 h under continuous heating at 55°C, compared to 9°C without
 890 encapsulation, which indicates that encapsulation methods should be developed and optimized
 891 for the long term durability of these THs.



892
 893 **Figure 8.** Main features of conductive polymer-based transparent heaters. a) Chemical structures of
 894 PEDOT and three main counter-ions forming respectively: PEDOT:PSS-EG, PEDOT:OTf and
 895 PEDOT:Sulf. b) Picture of a PEDOT-based TH illustrating its flexibility. c) Temperature increase of
 896 PEDOT:PSS-EG-based THs before and after 1000 bending cycles (9 mm radius of curvature) showing
 897 its good mechanical stability. d) Temperature increase versus areal power density for conductive
 898 polymer-based TH. b-d) Reproduced with permission.^[50] Copyright 2017, American Chemical Society.

899
 900 Another recently reported approach is based on the use of nanofibers of conductive polymers to form a
 901 mesh, which can be used as a TH. An effective and cost-friendly method to produce such nanofibers is
 902 electrospinning, which allows the polymer to be deposited onto any curved or flexible surface. Some

903 experiments were carried out on polycaprolactone/carbon black (PCL/CB), polyethylene
904 oxide/polyaniline (PEO/PANI) and PEO/PEDOT:PSS systems.^[85,171] The best results were obtained
905 with the PEO/PEDOT:PSS blend. These polymeric THs show moderate performances in terms of
906 heating properties, requiring a 60V bias to reach 70 °C, at 84 % transparency.^[85]

907 PEDOT:PSS films can also be patterned using a microfluidic post treatment with solvents. The
908 conductivity is locally boosted by several orders of magnitude, making it possible to obtain localized
909 heating with microscale resolution^[172].

910 These recent developments based on thin films of intrinsically highly conductive polymers open the way
911 to new high performance and purely organic THs.^[173]

912

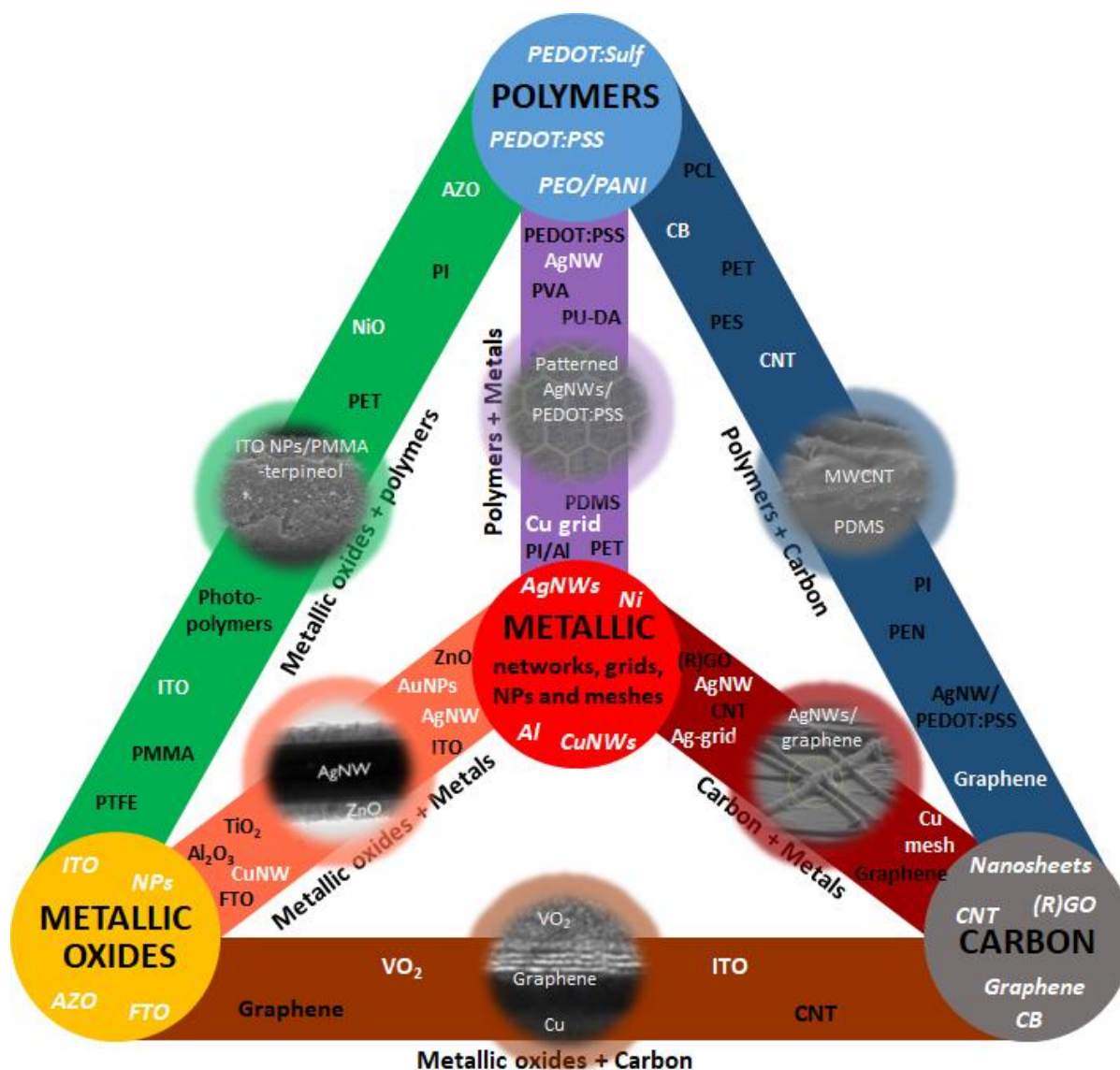
913 **3.5 Nanocomposites and hybrid transparent heaters**

914

915 THs have gained a constantly increasing attention in research and industry these past years with
916 a recent focus on multilayers, hybrids and nanocomposites. Matching materials with TH
917 requirements is promising since it combines the best properties and advantages of each material,
918 and generally offers much better performances than THs composed of a single material type.

919 In other words, each conductive nanomaterial (TCO, metallic-based materials, carbon-based
920 materials or conductive polymers) has its own advantages and disadvantages, but satisfying all
921 industrial requirements with a single material is nearly impossible. The combination of several
922 of these nanomaterials, however, can offer enhanced properties or better stability. This trend is
923 observed in other modern domains in advanced materials science. This can be illustrated with
924 the case of 1D carbon-based nanocomposites used in electrochemical energy storage devices;
925 these have attracted intensive research interests lately, as an effective way to store energy from
926 renewable energy sources. These aspects have been reviewed recently by Shi et al.^[174] who
927 showed that 1D carbon-based nanocomposites (where CNT are either embedded, coated,
928 encapsulated or supported) can be efficiently integrated into batteries and supercapacitors.

929 A large family of these hybrids for TH applications includes metallic nanowire networks or
930 grids/meshes coated with protective layers of graphene derivatives or TCOs. These composites
931 exhibit the very high electrical conductivity characteristic of metallic nanomaterials, and the
932 coatings offer higher electrical and thermal stability. Other structures include thin TCO layers
933 and metal nanowires ^[47], or MNWs combined with conductive polymers^[175]. The emerging
934 hybrids/nanocomposites based on nanomaterials open the way for flexible devices fabricated
935 using low-cost and up-scalable processes, and leads to a wide variety of modern applications
936 with futuristic shapes and everyday life uses. These nanomaterials can then be successfully
937 integrated into devices since they exhibit an interesting trade-off between electrical and
938 mechanical properties, stability, transparency and haze value. **Figure 9** illustrates the richness
939 and diversity of the materials investigated for TH applications. These materials have been
940 classified according to the main investigated TH technologies: they are composed of either the
941 four primary material types (metallic oxides, metals, conductive polymers and carbon) or of
942 hybrids/nanocomposites composed the combination of these primary materials. The primary
943 material is the main material, while the secondary material is usually present in lesser amounts,
944 and generally added afterwards. The main materials used in each case (primary and
945 hybrids/nanocomposites) are represented in white letters. Each picture illustrates an example of
946 a hybrid category: (from left to right, clockwise) 1) metallic oxides/polymers, 2)
947 polymers/metals, 3) polymers/carbon, 4) carbon/metals, 5) metallic oxides/carbon, 6) metallic
948 oxides/metals. The color code used in Figure 9 applies to the rest of the figures of this review.



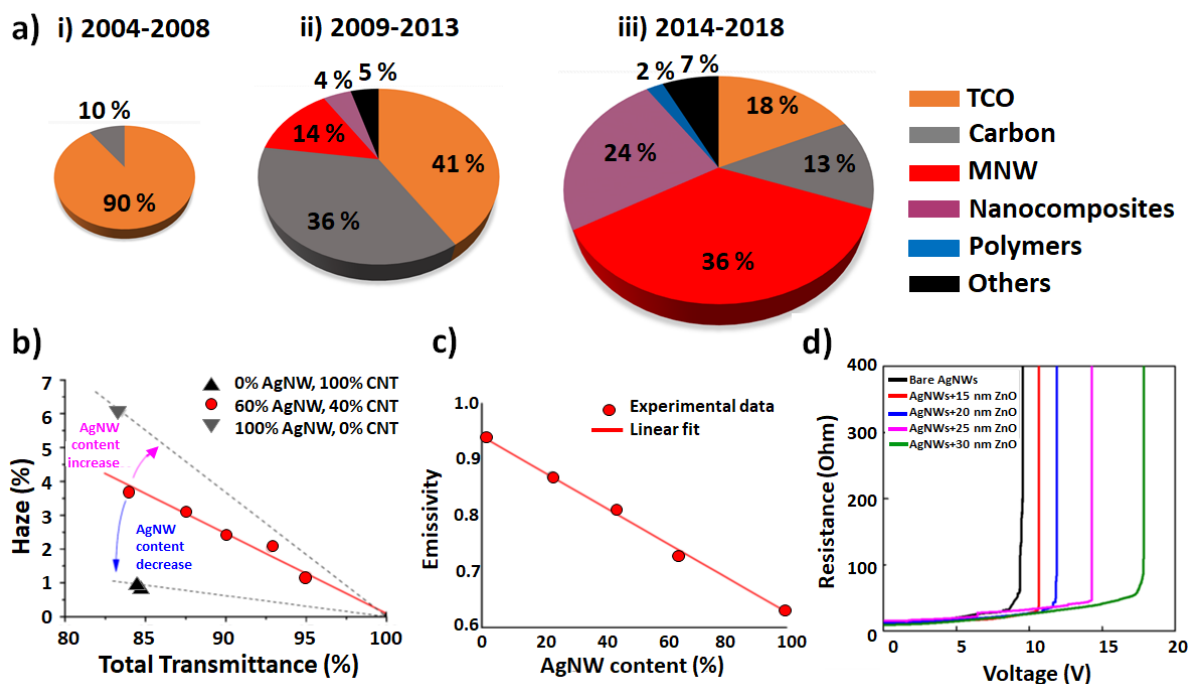
949

950 **Figure 9.** Schematic classification of main TH technologies investigated: they are either composed of
 951 the four primary material types (metallic oxides, metals, conductive polymers and carbon) or of
 952 hybrids/nanocomposites through combinations. This illustrates the richness and diversity of TH-related
 953 advanced materials. The main materials used in each case (primary and hybrid) are represented in white
 954 letters. Each picture illustrates an example of a hybrid category: (from left to right, clockwise) 1) metallic
 955 oxides/polymers; SEM image of an ITO NP/polymethyl methacrylate (PMMA)-terpineol mixture.
 956 Reproduced with permission.^[132] Copyright 2015, Elsevier. 2) polymers/metals; optical micrograph of
 957 printed AgNW/PEDOT:PSS composite grids with an hexagonal pattern. Reproduced with
 958 permission.^[176] Copyright 2019, MDPI. 3) polymers/carbon; cross-section SEM images of a
 959 MWCNT/polydimethylsiloxane (PDMS) bilayer film. Reproduced with permission.^[177] Copyright
 960 2015, Elsevier. 4) carbon/metals; Tilted cross-section SEM image of single-layer
 961 graphene/AgNW/glass. Reproduced with permission.^[178] Copyright 2019, John Wiley and Sons. 5)
 962 metallic oxides/carbon; HR-TEM of the cross section of graphene-supported VO₂ on a copper substrate
 963 which will eventually be etched. Reproduced with permission.^[53] Copyright 2013, American Chemical
 964 Society. 6) metallic oxides/metals; TEM image of a 30 nm thick ZnO-coated AgNW. Reproduced with
 965 permission.^[47] Copyright 2018, American Chemical Society.

966

967 To show the recent evolution of TH technologies related either to emerging materials or to
968 nanocomposites, we have investigated the relative number of publications per TH technology. **Figure**
969 **10a** shows, through pie-charts, the percentage of scientific articles associated to the different TH
970 technologies, gathered every 4 years since 2004. This shows that before 2008 TCOs related to TH were
971 almost the only technology reported in the literature, while carbon materials (graphene and CNTs) were
972 starting to be well studied. From 2009 on, metallic nanowires, meshes and grids have attracted much
973 more attention. These past years, nanocomposites/hybrids were the focus of many articles, and excellent
974 performances and stability have been reported. Of note, conductive polymer-based THs started to be
975 explored around 2017.^[50] The growing size of the pie-charts with time illustrates the fact that the number
976 of articles per year has been multiplied by 10 between the first period (2004-2008) and the more recent
977 one (2014-2018). It clearly shows the growing interest in THs from the scientific community, driven by
978 the industrial needs. In parallel, there is a strong industrial activity in the TH field, which is not reflected
979 in scientific publications due to intellectual property strategies. Similar trends as those shown in Figure
980 10a can be surveyed in terms of patent application numbers linked to TH technologies.

981 To illustrate the versatility of nanocomposites, Figure 10b and 10c illustrate a typical example where
982 properties can be tuned if the AgNW content is varied in hybrid conductive films composed of CNTs
983 and AgNWs.^[102] Figure 10b shows the influence of AgNW content on optical transmittance and haze
984 value, while Figure 10c shows the emissivity versus AgNW film content of similar film heaters prepared
985 by roll to-roll coating.^[102] Figure 10d shows the enhancement of the stability of AgNW networks thanks
986 to thin oxide layer (ZnO) coatings. The voltage failure observed during voltage ramps increases from 9
987 to 18 V for, respectively, bare AgNWs to 30 nm ZnO-coated AgNWs, showing a clear electrical stability
988 enhancement.^[47]



989

990 **Figure 10.** Emergence and examples of the assets of nanocomposite TH technologies. a) Pie-chart
 991 representing the percentage of scientific articles associated to the different TH technologies, showing
 992 that before 2008 mostly TCOs were mentioned in TH literature, while a small proportion of carbon
 993 materials (graphene and CNTs) were starting to be studied. Since 2009 MNW, meshes and grids have
 994 attracted much more attention. These past years, nanocomposites have been the focus of many articles,
 995 while conductive polymer-based THs have been explored since 2017. The pie-charts are growing with
 996 time to illustrate the fact that the number of articles per year has been multiplied by 10 between the first
 997 period (2004-2008) and the more recent one (2014-2018), demonstrating a clear growing interest in THs
 998 by the scientific community, driven by industrial needs (Sources: Scopus and Web of Science). b)
 999 Influence of AgNW content on optical transmittance and haze factor of hybrid conductive films
 1000 composed of CNTs and AgNWs. c) Emissivity versus AgNW film content of similar film heaters
 1001 prepared by roll to-roll coating. b,c) Reproduced with permission.^[102] Copyright 2013, Elsevier. d)
 1002 Variation of electrical resistance versus voltage for bare and ZnO-coated AgNW networks subjected to
 1003 voltage ramps of 0.1 V/min: the stability of the hybrid composite is clearly enhanced since the failure
 1004 voltage increases with ZnO thickness. Reproduced with permission.^[47] Copyright 2018, American
 1005 Chemical Society.

1006

1007 The next sections of 3.5 will focus in more detail on the properties of nanocomposites, discussed
 1008 per combinations of materials.

1009

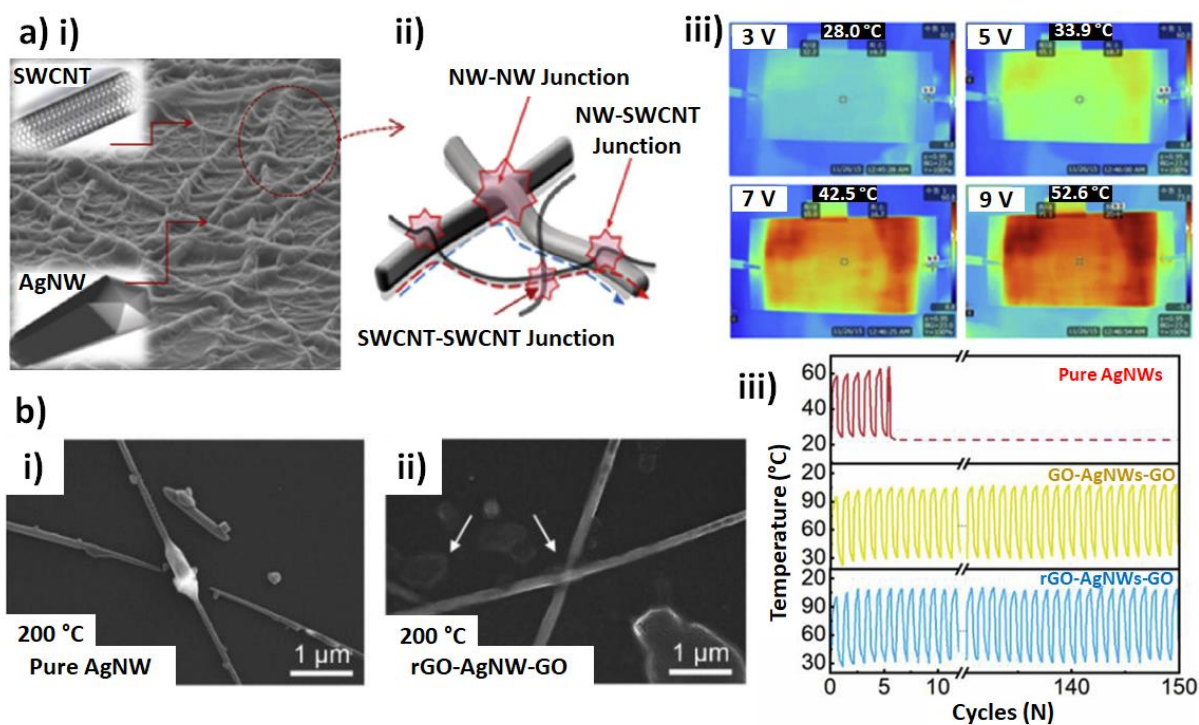
1010 **3.5.1 Higher thermal efficiency of metallic nanowire and carbon-based materials**

1011 Carbon-based materials and MNW hybrid materials have been widely developed for transparent
 1012 properties enhancements like haze tuning^[102,179,180], but also to improve stability^[181-183] or
 1013 adhesion.^[184] These hybrids are mainly comprised^[184] of 2D MNW networks (copper or silver)

1014 combined with CNTs, graphene, GO or rGO. As reported in section 3.2, carbon-based THs
1015 suffer from their poor conductivity at high levels of transparency. For heating applications,
1016 strong synergies are evidenced when combining the properties of carbon materials and MNWs
1017 for efficient, stable and highly flexible THs.

1018 The carbonaceous species (CNTs or Graphene) of the NW-based hybrids significantly improves
1019 stability and heat dissipation^[116] of the MNW networks for better thermal efficiency.^[185] Indeed,
1020 a more effective spreading of the heat with a small amount of SWCNTs improves the overall
1021 thermal stability of the NW network by improving resistance to current shocks.^[185] Moreover,
1022 the excellent thermal contact between nanowires and graphene, estimated at 0.5 m.K/W by
1023 Gupta et al. prevents Joule heating at the NW/NW junctions.^[186] Sadeque et al. focused their
1024 work on thermal transport behaviors in 2D networks of hybrid materials, especially
1025 graphene/AgNW composites.^[187] They disentangled contributions from local self-heating
1026 (hotspots) and heat spreading from the contacts, using thermorefectance measurements.^[187]

1027 **Figure 11a** shows SEM pictures of a CNT-AgNW hybrid heater. Highly stretchable and stable
1028 hybrid THs were developed, with a very low haze (under 1% at 95% transparency) and elasticity
1029 as high as 20%.^[80] As reported very recently by Wang *et al.*, a tri-layer film-based heater of
1030 rGO-AgNW-GO, as shown in Figure 11b, exhibits far better chemical, mechanical and thermal
1031 performances than pure AgNWs.^[188] They report a significant improvement in long-term
1032 stability, with fewer failures on the sandwich-structured film heater.



1033

1034 **Figure 11.** Carbon and MNW-based hybrid THs. a) AgNW-SWCNT hybrid composite layer on TPU: 1035 i) FESEM surface image of the hybrid composite layer. ii) schematic representation showing the current 1036 pathways. iii) IR thermal images of the SWCNT–AgNW hybrid TH, with a sheet resistance of 30 Ω /sq, 1037 under different applied input voltages (3, 5, 7 and 9 V). Reproduced with permission.^[80] Copyright 2018, 1038 Elsevier. b) Tri-layer rGO-AgNW-GO composite film i) SEM pictures of pure AgNWs, ii) tri-layer 1039 composite film heated at 200°C, iii) heating and cooling tests of pure AgNW, GO-AgNW-GO and rGO- 1040 AgNW-GO THs under ON/OFF current cycles of 60 s. Reproduced with permission.^[188] Copyright 1041 2019, Elsevier.

1042

1043 3.5.2 Adhesion enhancement within metallic nanowire/polymer hybrid transparent 1044 heaters

1045 As previously mentioned, polymers are extremely attractive in terms of flexibility/stretchability 1046 and processability. Nanocomposite materials relying on MNWs and polymers combine the high 1047 conductivity of a MNW network with the desirable mechanical properties of polymers, like 1048 flexibility,^[189] stretchability,^[190] and adhesion^[175].

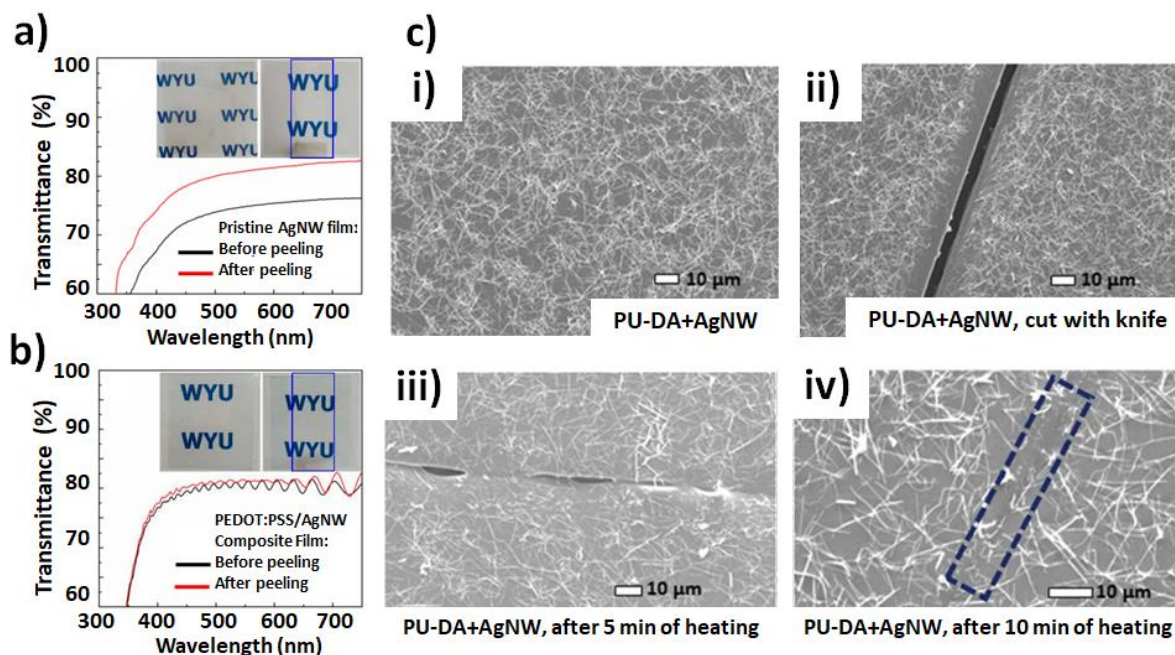
1049 Thanks to the addition of conducting elements in polymer matrices, it is possible to enhance 1050 the conductivity while preserving processability. Most of these composite-based THs take 1051 advantage of metallic nanofillers, often made of silver or copper. Nanospecies with high form 1052 factors are preferred, to favor percolation for the electron pathways. In particular, metallic

1053 nanowires can provide efficient networks at low densities, as described by the stick percolation
1054 theory.^[191,192] PEDOT:PSS, Polyimide (PI), polydimethylsiloxane (PDMS), PET, polyester
1055 (PE), poly(methyl methacrylate) PMMA, and even healable polyurethane (PU-DA) are the
1056 most reported matrices for the fabrication of composites for THs.^[79,112,114,175,189,193–204]
1057 Biopolymers like chitosan are interesting emerging materials for medical TH applications
1058 because of their biocompatibility and biodegradability.^[205] For composites, the choice of the
1059 polymer-conducting filler couple depends on the specific properties that are targeted. Polymers
1060 generally act as binders to ensure good contacts between nanoparticles and substrate, or they
1061 can serve as flexible/stretchable substrates to provide these properties to the system. They do
1062 not improve the heating properties, but are interesting nonetheless because of their optical
1063 properties (thin film transparency), their potential ability to allow the homogeneous dispersion
1064 of conducting nanoparticles, and for their mechanical performances. PEDOT:PSS is also often
1065 used as a host for the fabrication of conducting composites, and has mainly been used to
1066 improve the adhesion with the substrate. The comparison of film adhesion before and after
1067 peeling of 3M Scotch tape is demonstrated in **Figure 12a** and 12b for a pristine AgNW (Figure
1068 12a) and PEDOT:PSS composite film (Figure 12b).^[175] The optical transmittance (measured at
1069 550 nm) was increased from 75% to 81% for the AgNW film, while it remains at 79% for the
1070 composite film, demonstrating the enhanced adhesion of the composite.

1071 PEDOT:PSS can also enhance the conductivity by creating conductive pathways between
1072 spatially separated nanowires.^[206] In some cases, the conductive polymer can be doped with
1073 graphene to improve heating stability.^[116]

1074 Nearly all reported polymer/AgNW hybrid systems show similar performances with a maximal
1075 temperature of 100-150 °C, a transparency around 85 % at an operating voltage between 10 and
1076 40 V. Large differences in haze factor are observed, with values ranging from 3% ^[189] to 30
1077 %.^[194] Screen printing, doctor-blading and drop coating are the main methods reported for the
1078 deposition of AgNWs, which are then coated with the polymer.^[175,189,194] AgNWs can be

1079 embedded to improve the contact and stability in flexion, with a stable resistance after 1000
1080 bending cycles (with a 500 μm radius of curvature).^[189] Another way to stabilize the system is
1081 to add a thin transparent protective layer of poly(vinyl alcohol) (PVA) or insoluble PI.^[194,196]
1082 Healable polymers, based on the Diels-Alder reaction, can be cured by simple heat
1083 treatment.^[202] Figure 12c shows that after deliberate damage by a knife cut, the
1084 AgNW/polyurethane-based TH can heal and recover its original conductivity thanks to a simple
1085 heat treatment at 120 °C.^[202]
1086 Hybrid materials with a copper/alumina/PI combination are interesting, with a high and stable
1087 temperature of 300°C reached for a 10 V bias, associated with 91% transparency.^[201] Alumina
1088 limits the diffusion and oxidation of Cu, while PI is an effective binder to improve the adhesion
1089 strength between the Cu wires and the substrate. Heating stability was demonstrated for 100
1090 cycles with a substantial pulsed current of 1.5 A. Mechanical properties were investigated with
1091 bending (1000 cycles, 2 mm radius) and stretching (30 % stretchability on PDMS) experiments,
1092 and no significant change in conductance was observed. **Similar improvement of adhesion**
1093 **properties of AgNW networks to the substrate due to the use of PI was demonstrated by Lu et**
1094 **al.**^[204]



1095

1096 **Figure 12.** THs based on nanocomposites with AgNW networks and polymers. a) Peeling test
 1097 of a pristine AgNW film showing a large increase in optical transparency. b) Similar
 1098 experiment with AgNW and PEDOT:PSS composite showing no increase in optical
 1099 transparency, associated to a clear improvement in adhesion thanks to the polymer.
 1100 Reproduced with permission.^[175] Copyright 2017, MDPI. c) FESEM images of the
 1101 transparent, flexible and healable material with AgNWs and polymers: i) The healable TH as
 1102 deposited, ii) after a cut with a knife, iii) healing of the electrode at a temperature of 120 °C
 1103 for 5 min, and (iv) healing of the electrode at a temperature of 120 °C for 10 min. The dotted
 1104 box indicates the location of the previous cut. Reproduced with permission.^[202] Copyright
 1105 2017, Royal Society of Chemistry.

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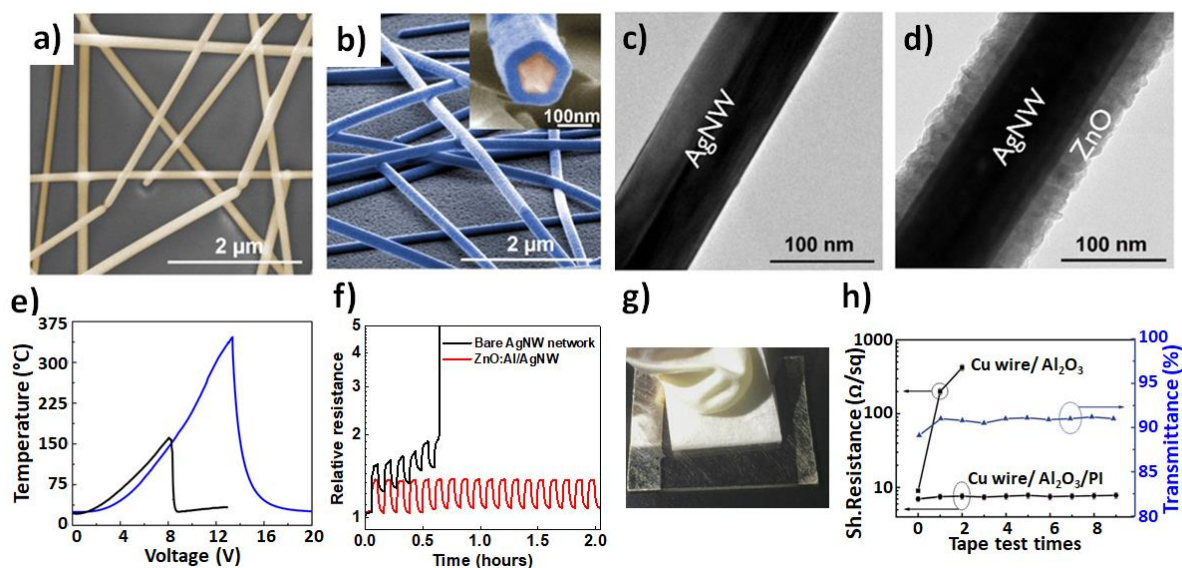
1107 3.5.3 Stability enhancement of metallic nanowires with oxide material

1108 Percolating MNW networks have been shown to act as efficient transparent electrodes^[20,33,34]
 1109 and can be used in solar cells^[40] and as THs^[42]. The most studied MNWs are AgNWs since
 1110 their synthesis and properties exhibit strong advantages: silver is the material with the highest
 1111 thermal and electrical conductivity at room temperature, and the synthesis of AgNWs is well-
 1112 mastered. However, these metallic nanowire networks suffer from stability issues. MNW
 1113 thermal instability leads to spheroidization (associated to the loss of the percolating nature of
 1114 the networks^[90]). Furthermore, electrical instability is observed when the networks undergo
 1115 electrical stress^[93,168]. CuNW networks are interesting^[30,31] since the price of Cu is much lower
 1116 than Ag. However, Cu is much more prone to oxidation than Ag and thus the chemical stability

1117 of CuNWs is a more critical issue. To enhance the stability of MNWs in general, several
1118 solutions have been investigated. The coating of MNWs by a thin oxide layer has shown clear
1119 improvements in stability. This strategy has been reported for AgNW/TiO₂^[46],
1120 AgNW/ZnO^[47,207], CuNW/Al₂O₃^[48,169], CuNW/ZnO.^[208] **Figure 13** shows SEM (a,b) and TEM
1121 (c,d) images of AgNW networks before (a,c) and after (b,d) the deposition of a thin layer of
1122 ZnO using atmospheric pressure spatial atomic layer deposition (AP-SALD)^[47]. This technique
1123 appears as an ideal approach to protect MNWs since it is a rapid, atmospheric and cheap method
1124 for thin film conformal deposition, and therefore does not compromise the low-temperature,
1125 atmospheric pressure fabrication of MNW networks.^[208–210] A 25 nm thick coating of ZnO
1126 drastically enhances the stability of the TH, as shown in Figure 13e.^[47] Figure 13f shows the
1127 relative electrical resistance of the bare AgNW network and the ZnO:Al/AgNW nanocomposite
1128 versus time when the samples were subjected to voltage ramp cycles (between 2 V and 6.5 V).
1129 The electrical stability is clearly enhanced thanks to the conformal coating when compared to
1130 bare AgNWs.^[208] Similarly, Tigan et al. recently reported an extensive study relating CuNW
1131 network density and oxide nature (Al₂O₃, ZnO) with electrical and optical properties, as well
1132 as stability. These authors were able to reach thermal stability up to 273 °C for CuNW with a
1133 thin Al₂O₃ coating, and a remarkably high heating rate of 14 °C/s.^[169]

1134 In addition to improving the network stability, oxide coatings give rise to materials with a much
1135 higher adhesion than bare nanowires. Figure 13g shows an optical picture of the peeling off test
1136 of a CuNW/Al₂O₃/polyimide(PI) composite film using 3M scotch tape.^[201] Figure 13h reports
1137 the variations in optical transmittance (blue) and sheet resistance (black) for Cu wire/Al₂O₃/PI
1138 (black circles) and Cu wire/Al₂O₃ (black square) network composite films versus the number
1139 of performed tape tests. The composite film (Cu wire/Al₂O₃/PI) clearly exhibits an enhanced
1140 adhesion compared to the Cu wire/Al₂O₃, which became insulating after the third tape test.^[201]

1141 Of note, an approach has recently been used to enhance the transmittance of AgNW networks
1142 coated with protective metal oxide bilayers thanks to an anti-reflective coating.^[211]



1143

1144 **Figure 13.** THs based on nanocomposites of MNWs and thin oxide layers. SEM (a,b) and TEM (c,d)
 1145 observations of AgNW before (a,c) and after (b,d) deposition of a thin layer of ZnO layer using
 1146 atmospheric pressure spatial atomic layer deposition (AP-SALD). A 25 nm thick ZnO coating drastically
 1147 enhances the electrical stability of the TH, as shown in e), with the measured temperature during a
 1148 voltage ramp for a bare and a coated silver nanowire network, in black and blue lines respectively. a-e)
 1149 Reproduced with permission.^[47] Copyright 2018, American Chemical Society. f) Relative electrical
 1150 resistance versus time of the bare AgNW network and ZnO:Al/AgNW nanocomposite when the samples
 1151 were subjected to voltage ramp cycles (between 2 V and 6.5 V): the electrical stability is enhanced
 1152 thanks to the conformal coating. Reproduced with permission.^[208] Copyright 2019, Royal Society of
 1153 Chemistry. g) Optical picture showing the peeling off test for the Cu wire/Al₂O₃/polyimide(PI)
 1154 composite film by 3M scotch tape. h) Variations of sheet resistance (black) versus the number of
 1155 performed tape tests for Cu wire/Al₂O₃/PI and for Cu wire/Al₂O₃ network composite films; optical
 1156 transmittance values (blue) Cu wire/Al₂O₃/PI are also plotted. g,h) Reproduced with permission.^[201]
 1157 Copyright 2016, Royal Society of Chemistry.

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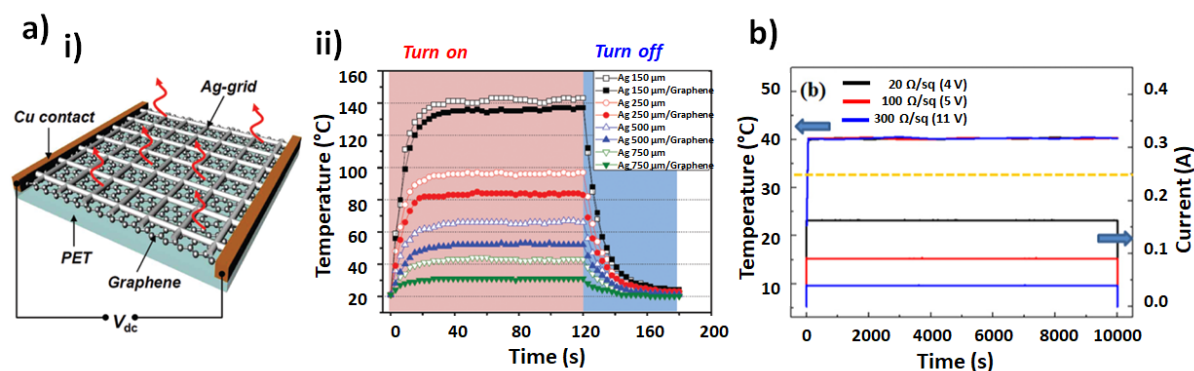
1159 While the positive effects of thin oxide coatings on the performance of MNW networks have
 1160 been reported several times, coating with metallic or oxide nanoparticles (NP) can also be an
 1161 efficient method. For example, Morgenstern et al. showed that full encapsulation of the AgNW
 1162 network by a layer of ZnO-NP drastically enhances thermal stability.^[207] Cheong demonstrated
 1163 that AgNW and AZO can lead to efficient and flexible THs: the AZO coating enables to reach
 1164 a higher average film temperature of 100 °C (30 °C higher than uncoated AgNWs) as well as a
 1165 greater heating uniformity.^[212] Cheng et al. also showed that AgNWs can be decorated with
 1166 gold nanoparticles, leading to a greatly enhanced thermal stability.^[213] Sharma et al.
 1167 demonstrated that highly stable THs can be obtained with AgNWs decorated with cobalt

1168 nanoparticles (CoNPs). It was found that an optimum AgNW-CoNP ratio of 50-50 wt% leads
 1169 to good performances of the corresponding TH, with a thermal stability up to 350 °C.^[214]

1170

1171 3.5.4 Metallic grids and transparent conductive oxides or graphene

1172 Hybrids based on metallic grids combined with graphene exhibit a superior electrical and
 1173 mechanical stability. Kim et al.^[148] fabricated copper grid meshes by photolithography and
 1174 deposited a graphene layer on top of the meshes (**Figure 14a**), while Kang et al.^[215] used
 1175 electro-hydrodynamic jet printing to write silver grids on a large-area graphene layer. In both
 1176 cases the hybrids showed improved and more uniform heating performances^[215] compared to
 1177 each separate material, even after thousands of bending or twisting cycles.^[148] In the case of the
 1178 Cu grid/graphene, the excellent flexibility is also due to the corona treatment of the PET
 1179 substrate. Another study on metallic grid-based hybrid THs combined Ag meshes with a thin
 1180 layer of ITO (Figure 14b). In this study, Kwon et al showed a 12% increase in optical
 1181 transmittance, followed by a lower power consumption compared to the as-deposited ITO
 1182 films^[149].



1183

1184 **Figure 14.** Transparent heaters from metallic grid-based hybrids. a) Ag-grid/graphene heaters: i)
 1185 schematic illustration of the Ag-grid/graphene film heater connected to Cu electrodes. The size of the
 1186 heating area was $5 \times 5 \text{ cm}^2$ and ii) time-dependent temperature response of the Ag-grid and Ag-grid
 1187 coated with graphene heaters. Reproduced with permission.^[215] Copyright 2015, Royal Society of
 1188 Chemistry. b) Ag mesh-ITO hybrid heaters with sheet resistances of 20, 100, and 300 Ω/sq . The
 1189 temperature remains very stable for 10,000 s while a voltage of 4, 5 and 11 volts is applied, respectively.
 1190 Reproduced with permission.^[149] Copyright 2014, IOP Publishing.

1191

1192 3.5.5 Transparent heaters based on metallic or transparent conductive oxide multilayers

1193 Other combinations of materials have been reported in the literature, including multilayers of
1194 TCOs or polymers with metallic thin films, or by combining different TCOs and nanoparticles.
1195 Several studies deal with the combination of a metallic thin film that is sandwiched between
1196 two TCO layers. Kim's group demonstrated that it is possible to make high-performance and
1197 flexible THs using continuous roll-to-roll (R2R) sputtering.^[51] In their studies, Ag or Cu was
1198 sputtered, from metallic targets, in between 40 nm thick ITO layers. They used a pilot scale
1199 system capable of coating 700 mm wide PET substrates at room temperature. In the case of
1200 ITO/Ag/ITO films, a transmittance of 88.2% and a sheet resistance of 3 Ω /sq were achieved.^[51]
1201 50 x 50 mm² THs were then fabricated, reaching a steady-state temperature of 100 °C by
1202 applying 5 V. In this case, the Ag layer was 12 nm thick and took around 100 s to reach 100
1203 °C. In the case of ITO/Cu/ITO layers, an optical transmittance of 73.9% and a sheet resistance
1204 of 11.8 Ω /sq were obtained.^[52] In this study, the best figure of merit was obtained for 12 nm
1205 thick Cu layers, and temperatures above 100 °C were obtained under a bias of 8 V. In another
1206 study, the ITO layers were replaced by InZnSiO, in combination with Ag, using the same R2R
1207 sputtering approach.^[216] The electrodes showed a transmittance of 91.91% and a sheet
1208 resistance of 7.83 Ω /sq for a 8 nm thick Ag layer. The electrodes reached 110 °C for a bias of
1209 only 2.4 V. The amorphous nature of the oxide yielded a high thermal stability upon cycling,
1210 as well as mechanical stability (no degradation of performance after 10,000 bending tests with
1211 a 10 mm bending radius).^[216] The same group presented a similar approach in which ITO was
1212 replaced by SnO₂ and the metal layer was composed of a AgPdCu alloy.^[217] In this case, these
1213 flexible In-free electrodes were deposited by thermal evaporation, and showed a minimum sheet
1214 resistance of 9.42 Ω /sq with transmittance values above 91% for 50 nm thick SnO₂ layers and
1215 a 10 nm thick metallic layer.^[217] The metallic layers alone showed a poorer performance than
1216 the tri-layer in terms of both conductivity and transmittance, due to the antireflective effects of

1217 the multiple coatings. THs made of SnO₂/AgPdCu/SnO₂ multilayers reached different
1218 temperatures for different SnO₂ thicknesses. For 10 nm thick oxide layers, temperatures above
1219 110 °C were obtained under a 5.5 V bias, with heating response times between 100 and 200
1220 seconds.^[217] Finally, in a similar approach, Roul *et al.* reported AZO/Ag/AZO electrodes made
1221 by sputtering, on PET substrates.^[218] The structural, electrical and optical properties were
1222 evaluated as a function of Ag layer thickness. The best results were obtained for a thickness of
1223 5 nm, for which temperatures above 100 °C were obtained for a bias voltage of 10 V.^[218] In
1224 another case of a multilayer transparent electrodes, Kang *et al.* proposed the study of
1225 polymer/Ag/polymer and polymer/Ag/inorganic (ITO or SiN_x) tri-layer electrodes.^[219] The
1226 electrodes were produced by an R2R sputtering system, and the addition of a fluorocarbon
1227 polymer led to a higher flexibility, with the electrodes sustaining bending up to a radius of 3
1228 mm, with a sheet resistance of less than 5 Ω/sq and a transmittance of 68%. The use of
1229 fluorocarbon polymer also yielded water-repelling electrodes, preventing wetting and removing
1230 contamination. THs based on fluorocarbon/Ag/SiN_x reached 180 °C for a bias voltage of 13
1231 V.^[219] Kim *et al.* have presented an asymmetric multilayer TH based on a GZO seed layer, an
1232 Ag metallic layer and a GZO optoelectronic control layer.^[220] The electrodes were deposited
1233 by sputtering at room temperature, and they showed an optimum sheet resistance of 5.4 Ω /sq
1234 for a transmittance of 81.6% (50 nm GZO/12 nm Ag/50 nm GZO). The electrodes were
1235 deposited on glass substrates of different thicknesses, in order to evaluate the effect of heat loss
1236 through the substrate. The temperature reached on the film and the substrate, as well as the
1237 rising time, both depended on the substrate thickness. Heat loss due to conduction needs to be
1238 considered for substrates ≥ 3 mm. A model is presented that allows the calculation of heating
1239 rates and deicing times.^[220] In a different approach, Im *et al.* proposed THs based of CNT sheets
1240 with granular metal (Pd).^[221] The addition of these metal particles boosted the heating efficiency
1241 by a factor of 3.6, from 99.9 to 27.3 °C cm²/W. This improvement is attributed to electron-
1242 lattice interaction and heat loss suppression. Finally, Hudaya *et al.* reported THs based on FTO

1243 with scattered metal nanodots (Cr, NiCr and Ni). The FTO layers were deposited by sputtering,
1244 while the metallic nanodots were deposited by electron cyclotron resonance CVD.^[222] The
1245 electrodes showed transmittance values over 85% and reached saturation temperatures over 80
1246 °C for a bias voltage of 12 V.

1247 These and other approaches, like TiO₂/Ag/TiO₂ multilayers, have been explored in recent
1248 years.^[223] While only the examples described above have been evaluated as THs, it is expected
1249 that more electrodes based on the combination of different materials will also be evaluated for
1250 TH applications.

1251

1252 **3.6 Synthetic comparison between the different TH technologies**

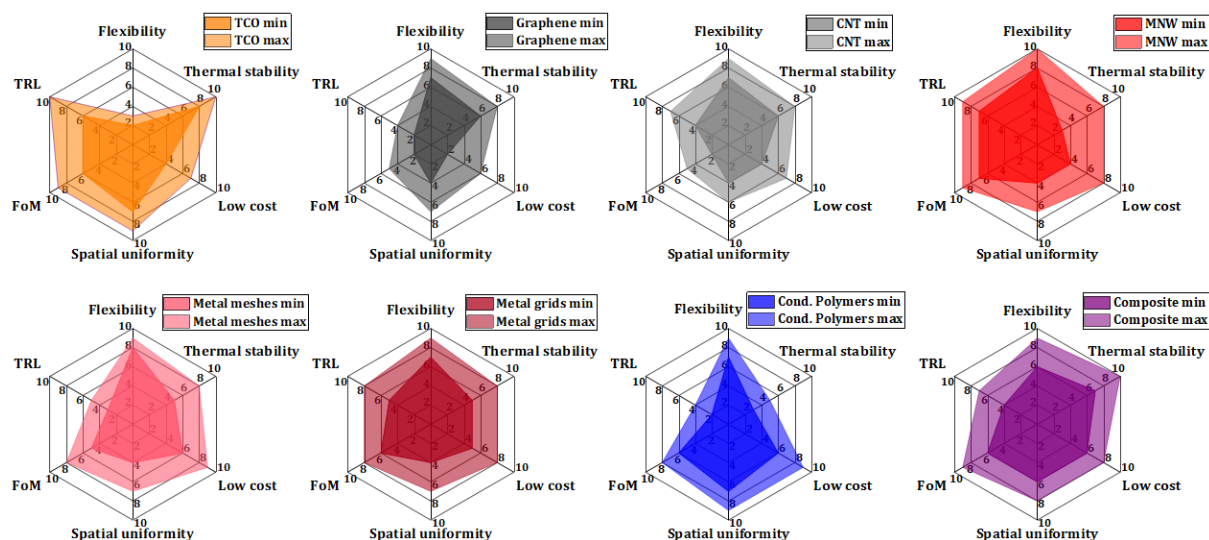
1253 As previously described, there are different TH technologies which exhibit diverse
1254 characteristics. We have briefly reminded the main features for each technology, and will
1255 compare them in more detail in this section. TCOs are the most investigated/used TH
1256 technology in industrial devices,^[10] and were discussed in section 3.1. They certainly are the
1257 most stable technology, at least in terms of electrical and thermal stability, but they are not
1258 compatible with flexible devices nor with solution-based fabrication processes. Moreover, due
1259 to indium scarcity, technologies using more abundant or cheaper materials, have been
1260 investigated.^[21] Carbon-based materials are mainly represented by carbon nanotubes and
1261 graphene, which have already been integrated in TH devices by several research teams (see
1262 section 3.2).^[27,61,143] Lately there has been a clear interest in metallic-based THs (as reported in
1263 section 3.3). MNW random networks have been well investigated these past years, in particular
1264 AgNW^[20,39] and to a lesser extent CuNW.^[48,66,169,224] Interesting properties in terms of TH
1265 behavior have been reported with this technology, along with promising flexibility and cost-
1266 effective solution process fabrication. MNW-based THs appear compatible with large scale
1267 industrial fabrication such as roll-to-roll technology.^[42,44,45] In parallel, metallic mesh networks
1268 and grids also exhibit good physical properties and constitute efficient THs.^[72,112,148] However,

1269 the thermal and electrical stability of these metallic-based THs can be a severe issue. However,
1270 as shown by Chen et al.,^[56] Cu based grids made from a Ag seed layer and a subsequent
1271 electroplating of Cu imprinted microgrooves exhibit very good performances. Indeed, sheet
1272 resistance down to 0.03 Ω /sq associated with a transmittance of 86% was demonstrated.
1273 Furthermore these TH exhibit good stability. The possibility to fabricate them by roll-to-roll
1274 manufacturing appears promising for industrial integration. Metal nanofibers present also
1275 interesting physical properties in recent studies.^[75,87] Additionally, very recent efforts have led
1276 to drastically improve the properties of conductive polymers^[49], reaching the conductivity of
1277 state-of-the-art FTO layers (i.e. $3 \cdot 10^{-4}$ S/cm)^[14]. By investigating different dopants for poly(3,4-
1278 ethylenedioxythiophene) (PEDOT)-based materials, Gueye et al. reported thin polymer films
1279 with a R_{sh} of 57 Ω /sq, a transparency of 87% and a very low haze factor (i.e. <1%). The use of
1280 these conductive polymers enables the fabrication of all-polymer-based THs with excellent
1281 performances^[50], with steady-state temperatures exceeding 100 °C when subjected to a 12 V
1282 bias.

1283 As described in section 3.5, the association of the different aforementioned materials leads to
1284 nanocomposites and/or hybrids, constituting a very rich family of TH technologies that offer a
1285 large panel of properties/performances with clearly enhanced electrical and thermal stabilities.
1286 The ongoing efforts by the community to fabricate, better understand and optimize THs is
1287 notably driven by the growing desire for low-cost, more stable and efficient THs. These efforts
1288 can efficiently address several challenges for many applications, the latter being described
1289 below in section 4.

1290 The comparison of these different technologies is represented in **Figure 15**, with several criteria
1291 being considered. It is worth mentioning that these criteria and the marks associated to each
1292 criterion and for each TH technology are subject to discussion, therefore only general trends
1293 should be considered. Depending on experimental TH synthesis and usage, a range of figures
1294 of merit with minimum and maximum values are proposed. Exceptions ruling out these trends

1295 do exist. The flexibility criterion refers to the capacity of a TH technology to withstand
1296 bendability or, for some applications, stretchability tests. TCOs are generally not flexible since
1297 oxides belong to the ceramic family, which are brittle materials (see Figure 7d), while other TH
1298 technologies are highly flexible. This is the case of all emerging TH technologies. Another
1299 critical issue is thermal stability: TCOs are very stable compared to other TH technologies. Thin
1300 oxide layers are even used as coatings for other TH technologies, forming efficient and stable
1301 nanocomposite THs. Conductive polymers are the least thermally stable among all TH
1302 technologies due to their organic nature. Nevertheless high temperatures (above 100°C) can be
1303 maintained for a long time, which is sufficient for most applications. The cost of a TH
1304 technology depends on several parameters, including the industrial production chain. The
1305 learning curves generally show a power law dependency between the cost of a device and the
1306 total cumulative production amount. Spatial uniformity is an application-dependent criterion.
1307 Homogeneous and continuous thin layers (such as TCOs, conductive polymers or some
1308 nanocomposites) are uniform by nature, while networks of carbon nanotubes or metallic
1309 nanowires, tiled graphene-based sheets or metallic grids can appear non-homogeneous, as
1310 demonstrated by the appearance of hot spots in the worst case.^[187] The use of nanocomposites
1311 combining both continuous and discontinuous THs can prevent this non-uniformity. Haacke's
1312 figure of merit (FoM) was used (Tr^{10}/R_{sh}): generally speaking, apart from graphene and CNT
1313 networks this FoM has rather high values for all TH technologies. Finally, the technological
1314 readiness level (TRL) criterion was used. The highest TRL value belongs to the TCO family,
1315 which has been investigated and used in industrial devices for several decades. The lowest TRL
1316 value is for the conductive polymers, for which the drastic progresses of conductivity making
1317 them very promising are only recent.^[49,50]



1318

1319 **Figure 15.** Comparison of THs fabricated with the different technologies. This figure shows the general
 1320 trends with six criteria (clockwise from the top): flexibility, thermal stability, low cost (of both material
 1321 and process), spatial uniformity, figure of merit (FoM) and technological readiness level (TRL).
 1322 Depending on the synthesis and usage of experimental THs, a range of figures of merit with minimum
 1323 and maximum values is proposed. The marks for all criteria for each TH technology are only general
 1324 indications, since the actual marks are application-dependent.

1325

1326 Other characteristics could also be of interest. This is the case for the haze factor, which should
 1327 be low (typically below 2 or 3%) when a TH is placed on windscreens, visors or displays to
 1328 ensure eye comfort (preventing blurriness). The haze factor is typically low for TCOs, while it
 1329 can vary drastically for other TH technologies. For instance, small MNW diameters are
 1330 preferred to decrease the haze factor^[96] of MNW-based THs. Recently, Ji et al. reported a study
 1331 of ultra-long copper nanofibers covered with a shell of carbon black, which can provide a high-
 1332 clarity view (i.e. with low haziness) associated to a transparency of 91% and a sheet resistance
 1333 of $0.8 \Omega/\text{sq}$.^[87] This once again shows that nanocomposite THs can exhibit excellent properties
 1334 through efficient combinations of key assets from different TH technologies.

1335

1336 4 Integration of transparent heaters in devices:

1337 As described above, THs concern numerous applications. TH fabrication is generally carried
 1338 out with the goal of implementation in a specific device and for a particular application. As
 1339 such, active material choice and device design must be considered according to specifications

1340 related to the operational use of the device. After pointing out some issues related to TH
1341 fabrication (part 4.1), we will describe examples of technical uses. The first one deals with THs
1342 for deicing, defrosting or defogging systems (4.2). Then we show how THs can be relevant for
1343 thermochromic devices (4.3), medical applications (4.4) and other niche applications (4.5).

1344

1345 **4.1 Integration of THs within devices: generalities and potential issues**

1346 Even though the intrinsic performances of the materials developed for THs are generally very
1347 good, their integration into functional devices can encounter some difficulties. Integration will
1348 depend on the nature of the active and support materials, and in general on the environment
1349 close to the heating film. In some cases, adhesion can be an issue if the deposited active layer
1350 does not stick well to the substrate. This can occur with metallic nanowires, which usually show
1351 limited adhesion and can be removed by a simple finger sweep. Layers of graphene- or PEDOT-
1352 based materials can be very thin (i.e. less than 20 nm) and thus very fragile and sensitive to
1353 mechanical stress. An encapsulating layer needs to be deposited on top of these materials to
1354 ensure a good adhesion to the surface, to avoid mechanical damage while preventing the release
1355 of the nanomaterials towards end-users. This encapsulation can be carried out through different
1356 techniques, like wet processes for transparent polymers, physical deposition of TCOs by atomic
1357 layer deposition, lamination with thin glass sheets or transparent adhesive films.

1358 As mentioned earlier, haziness must be finely controlled during the fabrication process since
1359 the haze value can vary significantly for some materials. Low haze values are mandatory for
1360 TH applications for windscreens or displays, whereas haziness may not be critical for other
1361 applications. This means that the fine control of the material itself (e.g. metallic nanowire
1362 diameter^[97] or layer thickness of carbon-based material) is crucial to reach the desired
1363 specifications and homogeneity on large surfaces. Depending of the TH application, tints
1364 induced by the materials should be considered (from a blue- or greenish hue for conductive

1365 polymers, blackish for CNTs, metallic greyish or a slight orange color for silver and copper
1366 nanowires, respectively, to yellowish with iridescence for TCOs).

1367 Despite their importance, electrical contacts are seldom mentioned in the reported works
1368 dealing with TH integration. The fabrication of good and reliable electrical contacts between
1369 the active layer and the voltage generator is usually not straightforward. Silver-based inks or
1370 pastes are often used for lab-scale demonstrations, but these materials are not always stable in
1371 the long term, and their homogeneous deposition can be tricky. Many other techniques and
1372 materials can be envisaged, like vacuum-deposited metals (gold, silver, copper, nickel, etc.),
1373 metallic ribbons or wires (usually copper-based materials), liquid metals (e.g. eutectic gallium-
1374 indium), or even materials with similar chemical natures to those used in THs, taking into
1375 account that these contact electrodes must be much less resistive than the active layers of the
1376 TH in order to avoid hotspots and Joule heating at unexpected locations.

1377 Beyond the nature of the electrical contacts, the geometry and patterns of contact electrodes are
1378 very important. They will define the heating zones. Depending on their design and voltage
1379 input, specific areas can be heated at different areal power densities. In a basic case study with
1380 two opposite electrodes on a square TH, the distance between the electrodes must be well
1381 designed with respect to the available bias supply. Indeed, the voltage must be increased when
1382 the distance between the electrodes is increased to keep good heating properties (generally at
1383 least a few hundreds of W/m^2). If this distance increases too much, then high voltages must be
1384 used, which can seriously damage the active materials.

1385 TH production should also consider the end-user application requirements. For highly flexible
1386 substrates for example, TCOs will not be suitable and polymer materials or metallic nanowires
1387 will be preferred. This choice of active material will also define the relevant and available
1388 deposition techniques, which are active material-dependent. For large area deposition
1389 techniques, special care should be taken to ensure homogeneous deposition, and ideally online
1390 analysis techniques should be implemented to check deposition uniformity.

1391

1392 **4.2 Deicing, defrosting and defogging**

1393 The first application of THs was to avoid condensation in aircraft windshields to increase
1394 visibility in warplanes during military actions. At that time, the TCM used was tin oxide , but
1395 in modern airplanes it has been replaced by ITO, which is more conductive and thus allows a
1396 lower operating voltage (24V).^[2]

1397 The heat produced by THs can also be used for defogging or defrosting applications. Defogging
1398 of car headlights is a recent need. Indeed, since the invention of cars, headlights have been
1399 based on incandescent bulbs, which inherently produce heat, preventing headlight condensation
1400 when they are on. Light-emitting diodes (LEDs) are now gradually replacing conventional
1401 incandescent lamps, because of their reduced energy consumption.^[225] Despite this obvious
1402 advantage, this new kind of headlight does not produce enough heat to avoid condensation or
1403 frosting at the surface of the headlights or inside the headlight housing. This situation creates a
1404 new risk, since fog or frost on the headlights can change light refraction and increase light
1405 diffusion, which degrades road illumination and thus visibility for the driver.

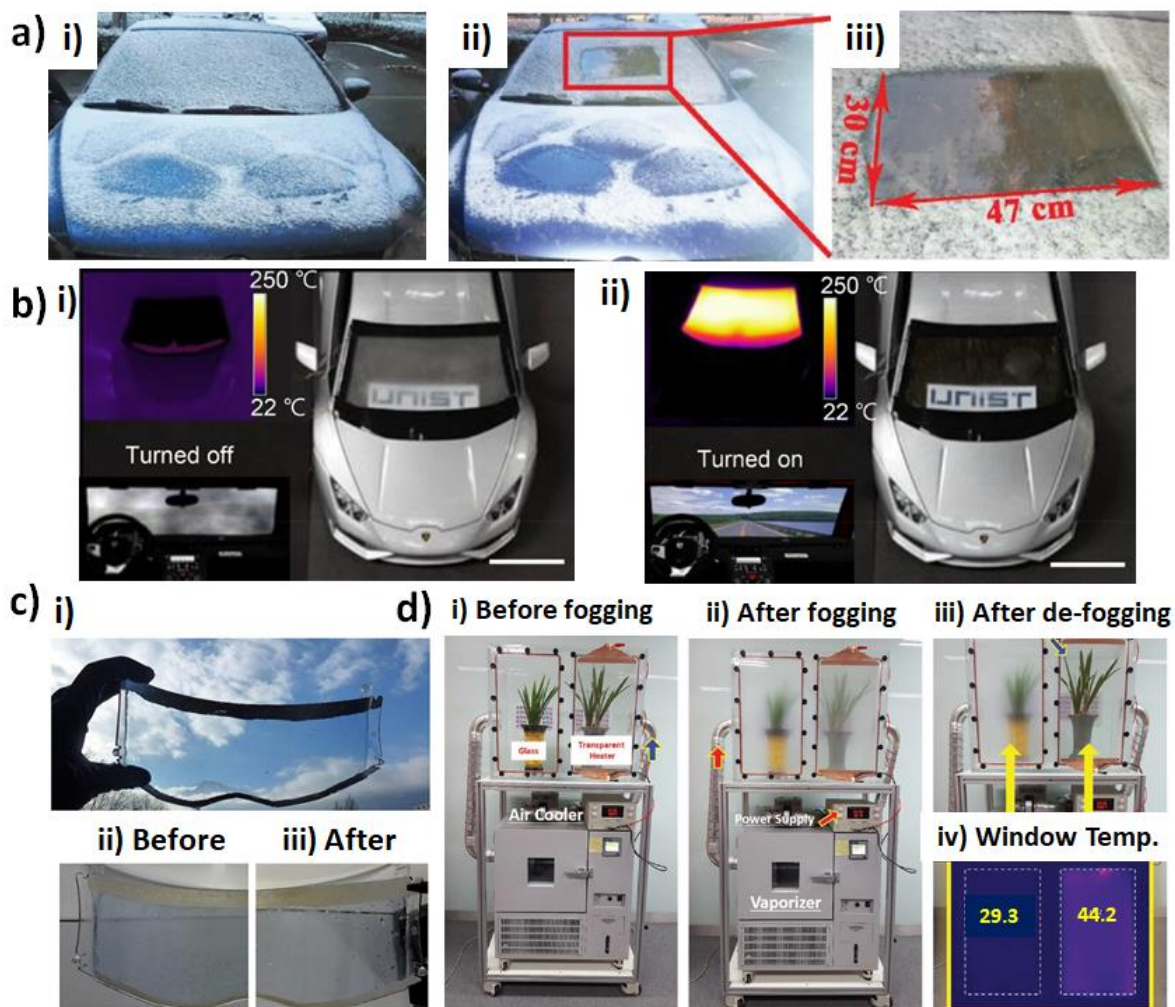
1406 There is a market for defogging devices based on THs in food distribution, with refrigerated
1407 showcases using transparent windows^[2]. Indeed, when products are refrigerated, there is a risk
1408 of condensation because of the temperature difference between the two faces of the case.
1409 Consumers not being able to see products behind the windows can be detrimental to the store;
1410 THs offer an efficient solution to this problem, and patents linked to this topic have existed
1411 since the 90s, with ITO technologies.^[226]

1412 LCD panels are used for outdoor applications. A limitation of LCD displays is liquid crystals
1413 freezing and electronic performance degradation at low temperatures^[227,228,61]. An ultra-thin
1414 film heater at the surface of the screen is an easy and lightweight method to heat the display
1415 and avoid degradation linked to low temperatures.

1416 For car windows (windshield and side windows) and external side mirrors, or even for
1417 motorcycle helmet visors, the operating voltage should ideally not exceed 12 V, which is the
1418 current standard voltage for cars and motorcycles. This is one of the reasons for the demand for
1419 new transparent coatings with lower resistances and similar transparency. The development of
1420 the 48 V vehicle will allow, in the near future, to reduce the pressure on the power management
1421 of large surface THs and will open up new prospects. Other reasons behind the demand for new
1422 transparent coatings concern flexibility and the ability to coat curved surfaces. As previously
1423 mentioned, some technologies meet these requirements, especially AgNWs, CNTs, graphene
1424 and conducting polymers.

1425 Many demo products have been fabricated, like defoggers/defrosters for car windows or side
1426 mirrors (**Figure 16a,b**), made of patterned AgNWs,^[229,230] AgNFs,^[231] Cu grids^[56] or Ni/Ag
1427 microgrids.^[195] A demo motorcycle visor (Figure 16c) dip-coated with PEDOT:PSS-EG was
1428 fabricated and can be defrosted in a few seconds with a low voltage.^[50] Zn-Sn-
1429 oxide(ZTO)/Ag/ZTO was also demonstrated to be of interest for small area defoggers (Figure
1430 16d), as well as for larger areas like the windshield of a commercial car.^[232] Since these systems
1431 require low voltages, even sport glasses/ski masks could integrate these new technologies in
1432 the coming years.

1433



1434

1435 **Figure 16.** Defrosting and defogging transparent heater applications. a) A car windshield i) before and
 1436 ii)-iii) after defrosting by applying 20 V for 5 min to a large-size Cu metal-mesh (30 x 47 cm²).
 1437 Reproduced with permission.^[56] Copyright 2019, John Wiley and Sons. b) Photographs of the Ag/Ag₂O-
 1438 NF/(index matching layer)IML heater-integrated automobile windshield at i) turn-off and ii) turn-on
 1439 modes. The applied dc bias was 6 V. The insets show a driver's view through the windshield (lower)
 1440 and an image captured with an IR camera displaying the temperature distribution of the windshield
 1441 (upper). Reproduced with permission.^[231] Copyright 2018, American Chemical Society. c) i) a
 1442 motorcycle visor with a PEDOT:PSS transparent heater, ii) iced in a freezer at -26 °C and iii) after
 1443 defrosting by the TH. Reproduced with permission.^[50] Copyright 2017, American Chemical Society. d)
 1444 Pictures describing the quality test of a Zn-Sn-oxide(ZTO)/Ag/ZTO transparent heater (52 x 31 cm²); i)
 1445 general setting of the test with a normal glass and transparent heater glass placed in front of each orchid
 1446 before running a test, ii) fog was generated on both windows using a moisturized hot air flow, iii)
 1447 defogging was carried out on the heater glass for 50 s at 12 V, and (iv) temperature profile of the two
 1448 glasses during defogging. Reproduced with permission.^[232] Copyright 2019, John Wiley and Sons.

1449

1450 4.3 Thermochromic applications

1451 The alteration of the color or transmittance of thermochromic materials induced by changes in
 1452 temperature can be used in a large variety of applications such as smart windows and green

1453 buildings, aerospace and military, textile and food packaging.^[233] Thermochromic smart
1454 windows are attractive because they are visibly transparent and can intelligently control the
1455 amount of solar heat (mainly in the near-infrared region) in response to changes in ambient
1456 temperature.^[234] Thermochromic applications are attracting more and more scientific and
1457 industrial interests, with efforts being devoted to their successful integration into modern
1458 devices. The research discussed in this part shows the Joule effect-based TH influence on
1459 thermochromic performance, the associated issues like layer adhesion, and the integration in
1460 devices. Vanadium oxide VO₂ materials are often presented, because they exhibit the greatest
1461 potential for thermochromic devices and energy-efficient systems^[235] thanks to their electronic
1462 structure modification from semi-conducting to metallic behavior when the temperature
1463 exceeds 68 °C. Emerging TCMs like CNTs^[236], graphene^[53], AgNWs^[109,200,237,238], conductive
1464 polymers^[50] and hybrids^[102,203] have been investigated as the heating elements.

1465 Liu et al.^[236] developed a CNT-based flexible microheater on PET for local heating into a
1466 thermochromic display, and tuned the thickness of the materials in order to optimize the
1467 thermochromic performance. A first approach was to decrease substrate thickness in order to
1468 obtain a good trade-off between mechanical robustness and thermal response. The thermal
1469 response of CNT-based films from room temperature to 100 °C was reduced to a few seconds
1470 thanks to the use of a 70 μm thick PET layer and with lower CNT coverage.^[236] Indeed, heat
1471 dissipation increases inversely with CNT coverage. Finally, a thermochromic display coupled
1472 to a driving circuit was made, and Chinese characters were displayed thanks to local heating by
1473 the CNT microheater on PET.

1474 In parallel, Kim et al.^[53] reported interesting progress related to the fabrication of flexible
1475 VO₂/Graphene-based thermochromic films for energy-saving windows. Graphene acts as a very
1476 thin (i.e. atomic film), flexible but robust substrate for the formation of stoichiometric VO₂
1477 crystals. The transfer of the graphene-supported VO₂ onto a plastic substrate enables the

1478 formation of a flexible thermochromic film which shows a decrease of in-house temperature
1479 under infrared irradiation in a mock-up house.

1480 In the case of AgNW-based THs, Li et al.^[237] studied the influence of AgNW networks on the
1481 VO₂ nanoparticle-based thermochromic performance. The infrared response of this
1482 VO₂/AgNW-based device can be controlled thanks to the applied voltage, and the dependence
1483 is shown to be highly stable and reversible. **Figure 17a** shows the square-like shape of the
1484 dynamic infrared response to the pulse voltage. The response of the VO₂/AgNW-based device
1485 exhibits a step variation. The transmittance in the infrared region can therefore quickly be
1486 altered when applying either rising or falling input voltage.

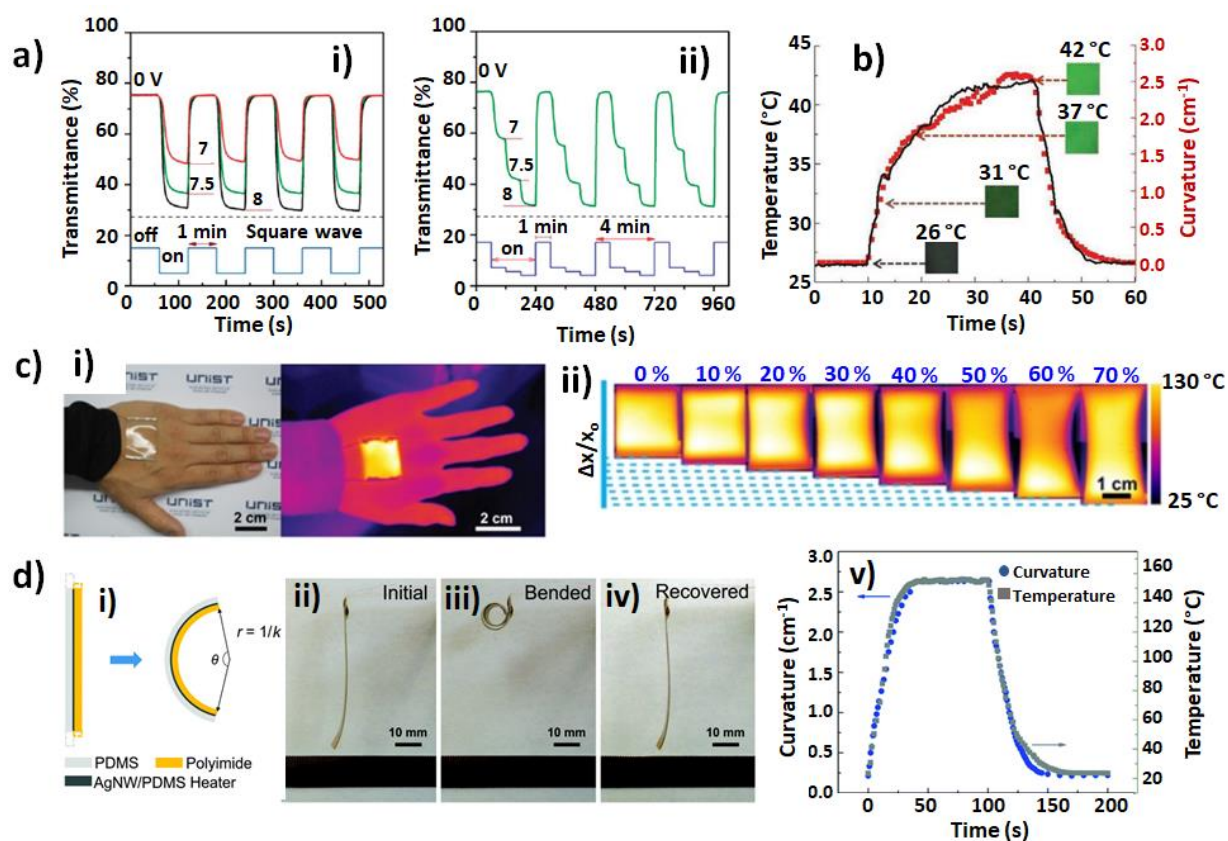
1487 Huang et al.^[238] fabricated a flexible AgNW/PI TH with faster and higher heating temperatures
1488 at lower power consumption compared to TCO heaters. The flexible and stable TH was
1489 successfully used in a thermochromic device. The obtained AgNW/PI-based TH exhibited a
1490 heating temperature of 96°C under a bias of 6V, and a response time of 40 seconds.^[238]

1491 Recently, Huang et al.^[200] fabricated a large-area flexible, transparent thermochromic window
1492 based on AgNW nylon-meshes. This thermochromic textile could be produced cheap and fast,
1493 i.e. 20 minutes for 7.5 m² and a cost of \$15.03.

1494 Another interesting and recent study presented by Kim et al.^[109] used AgNW-based THs as a
1495 color-shifting anisotropic soft actuator with a very large bending curvature of 2.5 cm⁻¹ at a low
1496 temperature of 40 °C. The transient behavior of the curvature and temperature of the color
1497 changing actuators based on AgNW Joule heating is shown in Figure 17b as well as digital
1498 camera images of the color of the actuator. The devices have demonstrated a superior long-term
1499 stability for more than 10,000 operating cycles. Shi et al.^[203] demonstrated a
1500 SiO₂/AgNW/colorless PI composite film heater with an improved transparency of 3.5 % due to
1501 the antireflective SiO₂ coating. The haze of both bare and SiO₂-coated AgNW/cPI films are the
1502 same, as well as their heating performance. The composite shows good mechanical properties,
1503 and was tested in a thermochromic device with a purple to blue color change after 10 s of

1504 applied voltage. Kim et al.^[102] fabricated a CNT/AgNW hybrid TH with reduced haze and
 1505 improved flexibility at 1.5 mm bending radius. The haze of the hybrid film is tuned by AgNW
 1506 content, and its heating performance is monitored by the color change of a thermochromic dye
 1507 inside a beaker wrapped with the CNT/AgNW TH film.

1508



1509

1510 **Figure 17.** Thermochemical, medical and other transparent heater applications. a) Infrared response at
 1511 1.5 mm of a VO₂ NP-electrothermochromic film device based on AgNWs upon input of a pulse voltage
 1512 with i) a square wave and ii) a square wave with a step variation. The dashed line denotes the lowest
 1513 transmittance at a constant voltage of 8 V. The pulse wave pattern and its application method are shown
 1514 below the dashed line, along with the wave parameters. Reproduced with permission.^[237] Copyright
 1515 2014, Royal Society of Chemistry. b) The transient behavior of the curvature and temperature of a color-
 1516 shifting anisotropic soft actuator based on an AgNW network TH. Insets are digital camera images of
 1517 the actuator's color changes with respect to temperature. Reproduced with permission.^[109] Copyright
 1518 2018, John Wiley and Sons. c) Transparent and wearable heaters using nanotrrough network of CuZr
 1519 metallic glasses; i) photograph and IR image of the heater attached to a human hand. The black strap is
 1520 the custom-made electronic band for a power supply and temperature controller. ii) IR images of the
 1521 CuZr nanotrrough heater under various tensile strains. Reproduced with permission.^[70] Copyright 2016,
 1522 American Chemical Society. d) Bending and heating performance of the PI/AgNW/PDMS bimorph
 1523 actuator; i) schematic of the electrothermal bimorph actuation mechanism. k: bending curvature; r:
 1524 radius of curvature, ii) the initial state, iii) the bent state with the maximum curvature and iv) the
 1525 recovered state of the U-shaped actuator. One end of the actuator is fixed and the other end can bend
 1526 freely and reversibly under an applied DC voltage of 4.5 V. v) Curvature and temperature of the actuator
 1527 as a function of time. Reproduced with permission.^[239] Copyright 2017, Royal Society of Chemistry.

1528

1529 **4.4 Transparent heaters for Medical applications**

1530 This last decade has seen the emergence of new flexible and stretchable electronics to fabricate
1531 sensors and actuators with properties similar to skin (namely deformation of up to 15 % and
1532 elastic modulus between 10 kPa and a few hundred kPa^[240]). These kinds of devices can be
1533 found under several names, namely “electronic skin”, “e-skin”, “epidermal electronics“ and
1534 “electronic tattoos”.^[241] They present the advantages of being skin-mountable and thus relevant
1535 for continuous health monitoring, drug delivery, thermotherapy, human motion detection,
1536 human-machine interfaces and soft robotics.^[241–243]

1537 Since 2013, Webb et al.^[244,245] have worked on the continuous thermal characterization of the
1538 skin by using ultrathin arrays of sensors and heaters. Combining sensing and heating allows to
1539 monitor physical and chemical parameters (like body temperature, glycemia, blood pressure
1540 and oxygen, elastic modulus of the skin^[241]) and potentially immediately diagnosing and
1541 delivering a medical treatment by cutaneous contact, keeping in mind that skin permeability or
1542 healing can be improved by local heating^[246].

1543 Epidermal drug delivery systems are attractive because of the reduced side effects of topical
1544 administration. Bagherifard et al.^[243] used flexible heaters in dermal patches to control the
1545 release rates of drugs encapsulated into a thermo-responsive hydrogel (N-Isopropylacrylamide,
1546 NIPAM).

1547 Currently, sensor heaters are generally made of a bilayer of chromium and gold^[243–245], which
1548 are not transparent. Nevertheless, the nanometric thickness of the circuit results in a quasi-
1549 transparent device and highlights this line of research.

1550 The most important application of electronic skins is thermotherapy, which is a new but
1551 expanding field. Indeed, heating pads are commonly used for a wide range of medical functions,
1552 like relieving pain^[247,248], preventing inflammation and improving blood circulation.^[121]

1553 Aside from pain relief, beneficial effects of a local heating treatment can be explained by the
1554 vasodilation, allowing blood vessels to supply more oxygen and nutrients to the surrounding
1555 area. Heating also prevents chronic inflammation by expelling inflammatory exudates.^[249]
1556 Moreover, heating pads can be useful in physiotherapy to help tendons, ligaments and muscles
1557 gain flexibility.^[250] The two currently available technical solutions for thermotherapy are heat
1558 packs and wraps.^[250,251] Heat packs are bulky and heavy and must be pre-heated in water or in
1559 a micro-wave, often compromising the fine control of the temperature. Heating wraps allow a
1560 better control of the temperature thanks to the Joule heating of resistors, but are usually rigid
1561 and heavy, which limits their wearability and their use in hospitals.^[23]
1562 New lightweight and autonomous devices combining a controlled temperature, fast response
1563 and high transparency are gaining interest. Using THs for thermotherapy pads would allow to
1564 see the heated parts of the body, potentially healing wounds, and to adjust more efficiently the
1565 treatment. Different techniques are under development to meet these requirements. The average
1566 values of temperature/voltage should be around 40-50 °C/3-5 V, to avoid burning the skin and
1567 to operate the devices with common batteries. Two methods are mostly studied: patterned
1568 nanocomposites and hybrid films with a network of metallic conductors and an elastomeric
1569 substrate.

1570 In 2015, Choi et al.^[23] developed a patterned nanocomposite made of AgNWs and a
1571 thermoplastic elastomer (styrene-butadiene-styrene, SBS). In order to obtain a highly
1572 conductive nanocomposite, a ligand-exchange reaction was carried out to homogeneously
1573 incorporate the AgNWs within the elastomeric matrix. This serpentine mesh-structure allows
1574 stable heating (+40 °C, 1 V) while being stretched (17% and 26% for extension or flexion of
1575 the wrist and the knee, respectively). The resistance remains stable after 5000 cycles at 30%
1576 strain and 48 h under UV exposure. Unfortunately, the device transparency value was not
1577 reported.

1578 Other techniques being developed use conductive networks based on MNWs or metallic
1579 glasses, coated on elastomeric substrates. CuZr metallic glasses on PDMS display excellent
1580 optoelectronic properties, with a resistance of 4 Ω /sq for 90% transparency, combined with a
1581 high stretchability (only 30% change in resistance for 70% strain, Figure 17c)).^[70] Moreover,
1582 a temperature of 60 °C can be reached for a bias of only 3 V. In terms of stability it is
1583 demonstrated that the heating performance of the film is stable for 10 days under relatively
1584 harsh conditions (85 °C for 85% RH). CuNW-based hybrids also present good performances,
1585 with 96 Ω /sq for 91% transparency, using a poly(methyl methacrylate) (PMMA) coating.^[252]
1586 To obtain a stretchable device, the elastomer Ecoflex® (blend of cellulose, lignin, poly(lactic
1587 acid), poly(hydroxy alkanate) and starch) was used as a replacement for PMMA, and enabled
1588 a stretching of 80% with a constant DC bias of 1.5 V. Under these conditions, however, the
1589 maximal reported temperature reached only 30 °C. If the stretching is kept low, a temperature
1590 of 50°C can be reached while applying 3 V, which is sufficient for thermotherapy. Percolated
1591 AgNW networks deposited on PDMS and encapsulated with PVA were shown to have adequate
1592 properties for thermotherapy pads, with high transparency (90%), low sheet resistance (20 Ω /sq
1593 and a low operating voltage (3.5 V to reach 45 °C)).^[121] Stability under severe thermal (80 °C)
1594 and humidity (80% RH, 45°C) conditions was demonstrated for an extended period of 6 months,
1595 in addition to mechanical stability over 10,000 bending cycles (1 mm radius).
1596 Recently, the impact of skin surface heating has been evaluated thanks to tests on porcine skin,
1597 to evaluate the efficacy of thermotherapy. A 12 °C temperature raise of the subcutaneous tissue
1598 (5 mm beneath the skin surface) was measured.^[190]
1599 Stretchable TCMs demonstrate promising potential for thermotherapy. The stretchability of
1600 THs for thermotherapy is an added value. Many research projects on these materials have
1601 emerged in recent years, often in strong relationship with the development of flexible and
1602 transparent electronics.^[253] Based on the growing interest in wearable devices and the wide

1603 range of medical applications, there is no doubt that the research on this topic will gain further
1604 momentum.

1605

1606 **4.5 Other niche applications**

1607 Besides the main applications previously described, THs are clearly interesting for other niche
1608 fields like actuators, gas sensors or refractive index tuning. Actuators are devices which are
1609 able to convert different types of energy, such as light^[254], electric fields^[255], magnetic
1610 fields^[256], pneumatic pressure^[257] or thermal energy, into mechanical energy. Among them,
1611 electrothermal actuators are based on either the thermal expansion of a single material or on the
1612 difference in thermal expansions between two materials. Their competitive advantages over
1613 other actuators are their low actuation voltage, as well as their lightweight and electrolyte-free
1614 design. Zhu et al. demonstrated the use of graphene in bimorph actuators.^[258] Graphene
1615 contracts upon heating due to a negative thermal expansion coefficient, which is opposite to the
1616 common behavior of nearly all materials. This asymmetric thermomechanical response leads to
1617 a large bimorph actuation. More recently, transparent electrothermal actuators using CNT-
1618 based THs^[259,260] and AgNW-based THs^[109,239] have been reported. Yao et al. demonstrated a
1619 remarkable 2.6 cm^{-1} curvature at a very low actuation voltage of 0.2 V/sq (4.5 V) in
1620 electrothermal actuators using AgNW THs (Figure 17d).^[239]

1621 Several studies mention the use of thermal stimuli to address different functions. Zhang et al.
1622 developed a transparency-switchable electrothermal actuator using aligned CNT-based
1623 THs.^[260] In this paper, the authors used a paraffin wax/polydimethylsiloxane composite. At
1624 room temperature, the composite is opaque due to the light scattering induced by the paraffin
1625 wax crystallites. Upon heating, actuation occurs simultaneously with wax melting, which
1626 results in a dramatic increase in transmittance. Kim et al. demonstrated the use of MNW-based
1627 THs for simultaneous actuation and thermochromic color change.^[109]

1628 Transparency becomes an important feature for gas sensors. Since heating gas sensors can
1629 improve their performances, the use of Joule heating with THs was reported to improve
1630 sensitivity and/or recovery time.^[62,261] Choi et al. developed graphene-based gas sensors, in
1631 which graphene was used for both sensing and heating.^[62] They reduced the recovery time of
1632 the NO₂ sensor by two orders of magnitude by heating the system up to 250°C. Similarly, Walia
1633 et al. improved the response time (from 41 to 13 s) and recovery time (from 112 to 35 s) at 1%
1634 H₂, with a moderate Joule heating at 75°C of the transparent conducting palladium network
1635 used for sensing.^[261]

1636 In another niche application, Heo et al. demonstrated the use of ITO-based THs for the
1637 development of lenticular lenses with a thermally tunable focus, using liquid crystals.^[262] The
1638 temperature can alter the birefringence of a liquid crystal-based lens by changing the refractive
1639 index between the active component and the polymer layer. Increasing the temperature from 25
1640 °C to 55 °C altered the focal length from 5.5 mm to 8.5 mm. These lenticular lenses have
1641 potential in optical devices like phone cameras.

1642 Finally Won et al.^[263] showed an original concept of stretchable kirigami TE consisting of
1643 ultrathin and flexible AgNWs/colorless polyimide cPI composites with laser patterned kirigami
1644 structure. A coating thin gold layer enables biocompatibility and enhances electrical stability.
1645 The laser patterning technique provides digital and rapid process (without patterning masks)
1646 allowing to design kirigami structures.^[263] This leads to achieve tunable stretchability, up to
1647 strain of 400%, which extends the scope of applications. Such a soft, thin and highly stretchable
1648 features can pave ways for multifunctional transparent and wearable electronic skin
1649 applications.

1650

1651 **5 Prospects, future challenges and conclusive remarks**

1652 Since the first use of THs approximately eighty years ago, tremendous progress has been made
1653 in this field. TCOs were the first materials developed and produced at the industrial scale to
1654 fabricate efficient THs. These materials have been highly improved over the past decades, and
1655 now reach outstanding properties, in particular thanks to an excellent transparency-conductivity
1656 trade-off. Although TCOs have been the materials of choice until now, new scientific
1657 breakthroughs and new market needs have opened the way for innovative developments,
1658 notably based on nano-enabled technologies. The driving forces to search for (improved)
1659 substitutes to TCOs not only rely on cost issues, but also on geostrategic considerations, which
1660 can be a game-changer, and on the technological evolution of devices. Many devices will
1661 require flexibility and stretchability (displays, PV cells, touch screens...), which requires new
1662 performances and abilities. The development of these transparent materials could offer an
1663 additional value to existing opaque film heaters and permit to see through the active layer. This
1664 could be of interest applications in health (*e.g.* patches for thermotherapy) or safety (*e.g.* control
1665 of heating elements such as automotive gas pre-heater pipes).

1666 Several relevant approaches appear very promising for TH production with improved
1667 functionalities. The recent development of nanomaterials has revealed unforeseen possibilities
1668 through the achievement of macroscopic performances relying on ordered or random
1669 assemblies of nanospecies, whether carbon-based or metallic. When electrically conductive
1670 nanoparticles are assembled on a surface above the percolation threshold, they give access to
1671 conductive surfaces at very low coverage values, which allows light to pass through, and to
1672 reach both high conductivity and high transparency. Another relevant possibility that needs to
1673 be further studied is the recent development based on the use of very thin films of highly
1674 conductive polymers. The performances are very promising, and these films have an
1675 intrinsically very low haze value.

1676 All these new technologies have managed to meet the expectations at the prototype stage, but
1677 certainly need further development to ensure reproducibility, cost-efficiency and stability at the
1678 industrial stage. Reproducibility mainly relies on the constant quality and chemical purity of
1679 the raw materials (CNTs, graphene, MNWs, polymers), but also on stable large-scale
1680 production tools and multiscale characterization techniques. Stability aspects are also
1681 particularly important, and they should be tackled while taking into account the targeted
1682 operational conditions. The stability will depend on many parameters like the structure of the
1683 device (including chemical compatibility with other layers), the applied voltage, the cyclability,
1684 high temperature long-term operating modes, and many others.

1685 Concerning the use of nanomaterials, an in-depth nanotoxicity assessment needs to be carried
1686 out to ensure the safe use for both the manufacturers' operators and the end-users. Some studies
1687 have already been reported^[97,264–268], but further understanding of all the possible toxicity
1688 aspects and long-term effects is needed.

1689 To conclude this review, the current production of THs still relies essentially on an “old”
1690 technology which has been improved upon over the years, i.e. TCOs. Many existing and future
1691 applications will keep using this technology because it is a reliable and well-proven process.
1692 However, various ongoing technical developments will provide THs with additional properties
1693 (controlled haze factor, flexibility, stretchability, low-cost deposition processes...). We expect
1694 that there will not be a single winner among them, but rather several new TH technologies that
1695 will find specific industrial applications in the near future.

1696

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1708

1709

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