

Irreversible Thermochemical Behavior in Gold and Silver Nanorod/Polymeric Ionic Liquid Nanocomposite Films

Christopher M. Tollan,[†] Rebeca Marcilla,^{†,‡} Jose A. Pomposo,[†] Javier Rodriguez,[†] Javier Aizpurua,[§] Jon Molina,^{||} and David Mecerreyes^{*,†}

New Materials Department, CIDETEC-Centre for Electrochemical Technologies, Parque Tecnológico de San Sebastián, Paseo Miramón 196, E-20009 Donostia-San Sebastián, Spain, DIPC-Donostia International Physics Center, Paseo Manuel de Lardizabal 4, E-20018 Donostia-San Sebastián, Spain, CEIT, Centro de Investigaciones Técnicas de Guipuzcoa, Donostia-San Sebastián, Spain, and CIC NANOGUNE Consolider, Donostia-San Sebastián, Spain

ABSTRACT The novel application of gold and silver nanorods as irreversible thermochemical dyes in polymeric ionic liquid (PIL) nanocomposites is proposed here. These materials have been synthesized by anion exchange of an imidazolium-based PIL in a solution that also contained gold nanorods. This resulted in the entrapment of the nanoobjects within a solid polymer precipitate. In this article, the effect of the temperature was studied in relation to the change of shape and, consequently, color of the gold or silver nanorods within the films. For the nanocomposites studied here, a maximum of two visual thermochemical transitions was observed for gold nanorods and up to three transitions were observed for silver nanorods.

KEYWORDS: silver nanorods • gold nanorods • thermochemical • nanocomposite • polymeric ionic liquid

INTRODUCTION

The unusual properties of metal nanoparticles have been, in recent years, subjected to the intense focus of the scientific community within the fields of optics, catalysts, nanophotonics, magnetism, and biotechnology. Nowadays, it is well-known that the properties of the metal nanoparticles are clearly material-, shape-, and size dependent. As an example, the optical properties of spherical nanoparticles of varying sizes are different. In addition, there are far more pronounced differences in the properties of spheres versus rods, ellipsoids, cubes, or stars (1–5). Among the different materials and shapes, gold and silver nanorods have received particular attention in relation to their unique optical properties. It is now well established that nanorods exhibit two surface plasmon resonance modes compared to spherical nanoparticles, which exhibit only one. One is the longitudinal surface plasmon mode that is associated with electron oscillations parallel to the rod-length axis, and the other is the transverse surface plasmon mode that is associated with electron oscillations perpendicular to the rod-length axis. It is noted that, because of the difference in the

dielectric function of silver and gold in combination with the dielectric function of the surrounding medium (6), the surface plasmon resonance absorptions of silver are of a shorter wavelength than those found for gold for any given size or shape of nanoparticle. Both experimental and theoretical studies have shown that there is a linear dependence of the longitudinal plasmon wavelength of both gold and silver nanorods upon their length-to-diameter aspect ratio. Consequently, a slight variation in the aspect ratio of the nanorods can induce distinct color changes. Owing to these attractive properties, nanorods have been demonstrated to function as scattering (7) and two photon luminescent chromophores (8, 9) for biological imaging, biological sensors (10–12), carriers for drug delivery (13), and therapeutic agents for photothermal cancer treatment (7). In this article, the novel application of gold and silver nanorods as dyes in irreversible thermochemical films is presented.

Thermochemicalism, the change of color with temperature, is a phenomenon that finds technological applications in thermometers (fever indicators, gadgets, design applications, etc.), temperature sensors for safety, laser marking, or warning signals. Many different compounds such as liquid crystals (14), conjugated oligomers (15), inorganic oxides (16), or leuco dyes (17) are well-known to exhibit the ability to change color reversibly with temperature. However, thermochemical dyes, which show irreversible color changes on heating, are rare and are usually based on organic compounds (18). To date, gold nanorods show little or no reaction with molecular oxygen at elevated temperatures or after prolonged irradiation. In contrast, many complex organic dyes slowly degrade under such conditions. The goal

* Address correspondence to dmecerreyes@cidetec.es. Phone: 34943309022. Fax: 34943309136.

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[†] CIDETEC-Centre for Electrochemical Technologies, Parque Tecnológico de San Sebastián.

[‡] CIC NANOGUNE Consolider.

[§] DIPC-Donostia International Physics Center.

^{||} CEIT, Centro de Investigaciones Técnicas de Guipuzcoa. Current address: IMDEA-Materiales, c/Professor Aranguren s/n, 28040 Madrid, Spain.

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Scheme 1



of this article is to report the high-temperature irreversible thermochromic behavior of gold and silver nanorod/polymeric ionic liquid (PIL) nanocomposite films and the association of this effect with a change of the shape of the nanorods within these composites at elevated temperatures (Scheme 1).

EXPERIMENTAL SECTION

Materials. Ascorbic acid ($\geq 99.0\%$), cetyltrimethylammonium bromide (CTAB; $\geq 98\%$), chloroauric acid (HAuCl_4 ; 49% as Au), lithium bis(trifluoromethanesulfonyl)imide (97%), sodium borohydride (99%), poly(vinylpyrrolidone) ($M_w = 1\,300\,000$ g/mol), and poly(vinyl alcohol) (99% + hydrolyzed) were all bought from Sigma-Aldrich Quimica SA. A 0.1 M silver chloride solution was purchased from Quimibacter SL.

Methods. UV–vis spectroscopy was performed using a Jasco V-570 UV–vis–NIR spectrophotometer.

Synthesis of Gold Nanorods. The gold nanorod synthesis was adapted from a general procedure reported previously (2). All solutions were made in distilled water. A 0.2 M solution of CTAB (29.10 cm^3) was added to a glass vial (30 cm^3). To this was added a 0.1 M HAuCl_4 solution (0.30 cm^3) and a 0.1 M silver chloride solution (0.06 cm^3) followed by mixing by repeated inversion. This gave an orange solution. A 0.2 M ascorbic acid solution was then added (0.30 cm^3) and again mixed by repeated inversion to give a colorless solution. Finally a freshly prepared 0.001 M sodium borohydride solution (0.03 cm^3) was added and mixed once again by repeated inversion (10 s). A deep purple color began to appear within 5 min. The solution was then allowed to stand for 1 h, after which time the solution was centrifuged (40 min, 50 000 Hz). The pale-pink supernatant was discarded to leave a dark-purple/black precipitate. The precipitate was redispersed in distilled water (20 cm^3), and the procedure was repeated. The resulting precipitate was redispersed in distilled water and made up to a final volume of 60 cm^3 .

Synthesis of Silver Seeds. The silver seed synthesis was reported previously (19). All solutions were made in distilled water. A 0.25 mM solution of trisodium citrate (20 cm^3) was added to a glass vial (30 cm^3). To this was added a 0.1 M silver nitrate solution (0.05 cm^3) followed by a 0.01 M sodium borohydride solution (0.6 cm^3). The solution was immediately shaken vigorously by hand for 30 s and then allowed to stand for 30 min before being used for nanorod growth.

Synthesis of Silver Nanorods. The silver nanorod synthesis was reported previously (19). All solutions were made in distilled water. A 0.08 M solution of CTAB (30 cm^3) was added to a glass vial (50 cm^3). To this was added a 0.1 M silver nitrate solution (0.075 cm^3) and a 0.1 M ascorbic acid solution (1.5 cm^3) followed by mixing by repeated inversion. The seed solution was then added (0.30 cm^3) and again mixed by repeated inversion to give a pale-yellow solution. Finally, a 1 M sodium hydroxide solution (0.3 cm^3) was added and mixed once again by repeated inversion (10 s). A strong yellow color rapidly appeared within 1 min, which then changed through orange, red, and finally purple/blue. A gray suspension was also observed in the mixture. The solution was then allowed to stand for 1 h, after which time the solution was centrifuged (30 min, 40 000 Hz). The supernatant was discarded to leave a dark-purple/black precipitate. The precipitate was redispersed in distilled water (20 cm^3).

Fabrication of Gold and Silver Nanorods/Poly(nanocomposites). The gold (or silver) nanorod solution (5.0 cm^3) prepared above was placed in a glass vial (30 cm^3). To this was added an aqueous solution of PIL (0.65 g in 5 cm^3), giving a clear purple solution. An aqueous lithium bis(trifluoromethanesulfonyl)imide solution (1.13 g in 2 cm^3) was then added dropwise with stirring to give a pale-purple precipitate. The remaining colorless liquid was decanted off, and the solid was dried under a stream of air at room temperature for 16 h.

Preparation of PIL Nanocomposite Films and Subsequent Heating to Bring about Thermochromic Activity. The solid obtained from the above procedure was dissolved in acetone (5.2 cm^3), and films were cast onto glass microscope slides from this purple-colored solution. The slides were then placed on a hot plate, which had been heated to a predetermined temperature, for 5 min.

RESULTS AND DISCUSSION

The synthesis of the gold nanorods was found to be a valuable and reproducible method. The synthesis of silver nanorods, on the other hand, was more complicated and required a considerable amount of technique in order to obtain the nanorods in a reasonable yield. It is also noted that during purification of the nanorods more than one centrifuge cycle of the silver nanorods or excessive dilution of surfactant solutions containing the silver rods led to destabilization of the nanorod shape, resulting in a color change. This was not found to occur with the gold nanorods, indicating that they are more stable than their silver counterparts. Gold and silver nanorod/PIL nanocomposite films were fabricated as previously reported (20). First, a solution of chemically synthesized nanorods was coagulated with poly(1-vinyl-3-ethylimidazolium bromide) by anion exchange of the bromide ion using bis(trifluoromethanesulfonyl)imide)lithium salt. By this method, a gold nanorod/poly(1-vinyl-3-ethylimidazolium) bis(trifluoromethanesulfonyl)imide) powder was obtained in quantitative yield. This powder was dissolved in acetone, and free-standing nanocomposite films were obtained by casting, warming up, and subsequent evaporation of the organic solvent. At this point, it is worth remembering that several groups have already reported that nonspherical gold nanoparticles can undergo laser-irradiation-induced shape and size transformations (21, 22). After irradiation, the gold nanorods were converted into more stable isotropic particles such as spheres. This irradiation effect was also demonstrated in nanocomposite films of gold nanorods and poly(vinyl alcohol) (22, 23). Using a pump–probe technique based on two asynchronously locked femtosecond lasers, it has been demonstrated that at a temperature of $104\text{ }^\circ\text{C}$ the damping rate and phase change abruptly, indicating a structural transition in the particle, which is explained as the onset of surface melting (24). The reason that the process of shape change upon surface melting of the nanorods results in a spherical shape is due to spheres being the shape in which surface tension is minimized; that

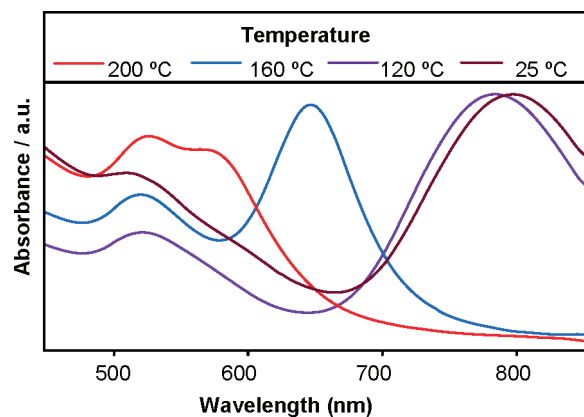


FIGURE 1. UV-vis-NIR spectra of gold nanorod/poly(1-vinyl-3-ethylimidazolium) bis(trifluoromethanesulfonimide) films heated to various temperatures up to 200 °C.

is, it has the lowest surface area to volume ratio. The thermal transformation of gold nanorods into spheres has been described in solution at temperatures in the range of 25–160 °C, which depend on the solvent, the stability of the micellar solutions, and the mean aspect ratio of the nanorods (25, 26). There are also reports of thermal transformation of nanorods when deposited on a glass slide as a submonolayer (27). To our knowledge, there has been no previous report on the thermally induced shape change of metal nanorods inside polymer matrixes and the application as thermochromic materials proposed here. Thus, in this work, gold or silver nanorod/poly(1-vinyl-3-ethylimidazolium) bis(trifluoromethanesulfonimide) films were heated to different temperatures and the UV spectra of the films were recorded (Figure 1). As expected, the spectrum of the initial gold nanocomposite film at 25 °C displays two resonance peaks, one small peak at 510 nm and a second peak at 796 nm associated with the initial gold nanorod plasmon resonances with an aspect ratio of 3.5. Upon heating to 160 °C, a clear shift of the longitudinal surface plasmon mode from 796 to 646 nm is observed. At 200 °C, the longitudinal plasmon mode almost disappeared and only one wide peak between 500 and 600 nm was observed, indicating that a change in the nanorod shape had occurred. Interestingly, this trend is similar to the nanorod-to-sphere transition observed in the irradiation-induced shape transition of gold nanorods in polymer films.

In order to confirm the above speculation, we performed transmission electron microscopy (TEM) studies on the gold nanorod/poly(1-vinyl-3-ethylimidazolium) bis(trifluoromethanesulfonimide) films treated at 160 and 200 °C, respectively. As observed in Figure 2 and in accordance with the UV spectra of Figure 1, the color of the films changed from violet (25 °C) to blue (160 °C) and finally to pink (200 °C). TEM results demonstrated that the initial gold nanorods with an aspect ratio of 3.5 are transformed into nanorods with a smaller aspect ratio of 2.0 at 160 °C (blue) and almost spherical particles at 200 °C (pink). The TEM images of the nanorods correspond closely to the theoretical aspect ratios expected from a maximum of the peaks of the UV spectra, as shown in Figure 3. In other words, gold nanorods are gradually transformed into spheres upon heating and, consequently, the color of the polymer films changes. This

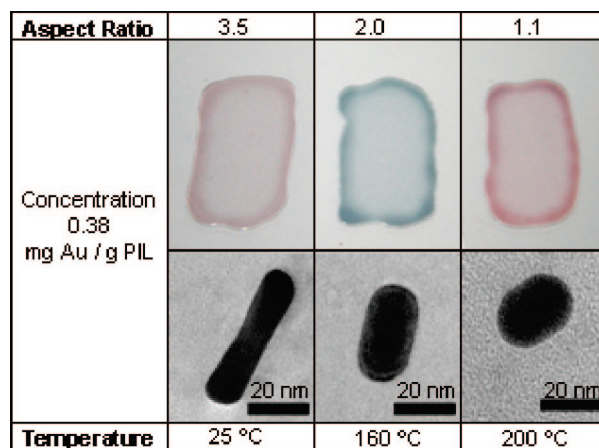


FIGURE 2. Photographs of gold nanorod/poly(1-vinyl-3-ethylimidazolium) bis(trifluoromethanesulfonimide) films at different temperatures and TEM images of the gold nanorods contained within the films.

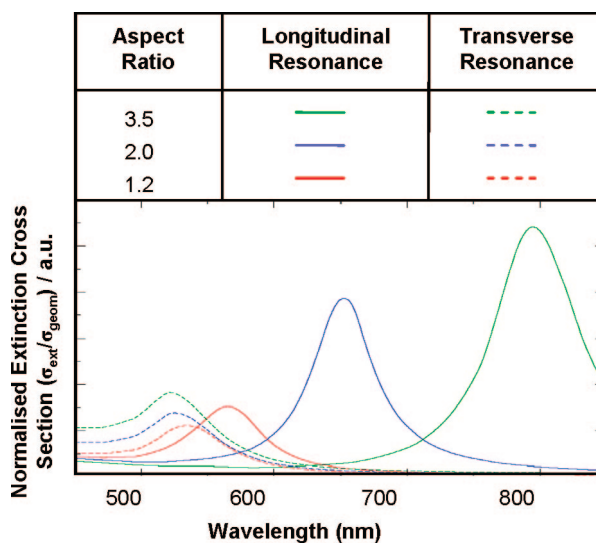


FIGURE 3. Theoretical plasmon resonances for gold nanorods of various aspect ratios. The theoretical values correspond well with the experimental results obtained in Figure 1.

thermally induced visual color change is 2-fold (violet to blue and blue to pink) and irreversible because upon cooling the gold spheres keep their shape and the films their corresponding color.

A similar study of silver nanorod films has also been carried out using the same techniques for trapping of the nanorods within the poly(1-vinyl-3-ethylimidazolium) bis(trifluoromethanesulfonimide) matrix as those used for the gold nanorods. It is again noted here that the dielectric functions of silver and gold are different, and as a result, the surface plasmon resonance arising from the interaction of light with these electrons results in extinction (absorption and scattering) at different wavelengths (28). For example, with spherical nanoparticles, the single surface plasmon resonance for gold is around 500–550 nm, whereas the surface plasmon resonance for silver is at a shorter wavelength of 400–450 nm, giving rise to the different colors of red and yellow, respectively. This difference in color between the two metals is a general rule for all silver and gold nanoobjects, with silver nanorods giving both longitudinal

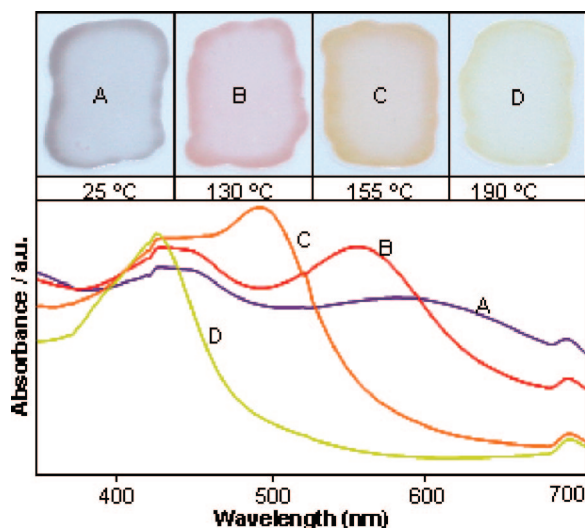


FIGURE 4. Photographs of the silver nanorod/poly(1-vinyl-3-ethylimidazolium) bis(trifluoromethanesulfonimide) films heated to various temperatures up to 190 °C and the corresponding UV-vis spectra.

and transverse surface plasmon resonances at shorter wavelengths than gold nanorods of an equivalent size. As far as irreversible thermochromic dyes are concerned, this holds a great advantage because a wider ranging color gamut can be obtained as compared to the use of just one metal. As shown in Figure 4, the use of silver nanorods allows for the fabrication of thermochromic materials with colors ranging from purple/red through orange to yellow with the appearance of three visible thermochromic transitions, as opposed to the two transitions present for the materials formed using gold nanorods. It is noted that these color transitions refer to what is visually perceived; at a spectroscopic level, there is a continuous and gradual shift in the wavelength at which the materials absorb light as the nanorods gradually change shape. The use of silver expands the range of colors, with some overlap, that can be incorporated into the materials, going from purples, blues, and reds found in the gold thermochromic materials to purple, red, orange, and yellow with the silver nanocomposites. Along with the expansion of the color range upon use of additional metals, there is also scope for expanding the range of temperatures at which the thermochromic transitions occur. The gold transitions were found to occur at 160 and 200 °C, whereas in silver, the transitions are as follows; purple to red at 130 °C, red to orange at 155 °C, and orange to yellow at 190 °C. Therefore, by using a second metal, the temperature range for the thermochromic transition has been broadened to lower temperatures by an additional 30 °C.

As stated in the Methods section of this article, all observed visual color changes occur within 5 min of the composite film being placed on a hot plate at the quoted temperature. This does not take into account the kinetic effect of elevated temperatures over an extended period of time. In order to investigate such kinetic effects in relation to time, a number of silver nanorod films were fabricated and then placed in an oven at 100 °C. The first film was removed after 1 min and rapidly cooled under a stream of

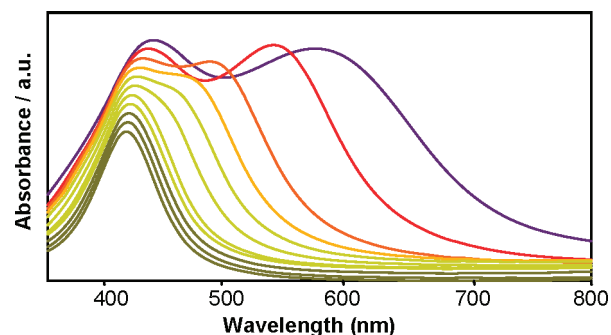


FIGURE 5. Diagram showing the UV-vis spectra of the silver nanocomposite films after heating to 100 °C over a time period of 300 min. Each spectral trace was measured at 30 min intervals.

air; this procedure of the removal and cooling of individual films from the oven was repeated at 30 min intervals until the final film was removed from the oven after 300 min. The UV spectra of these films were recorded and are shown in Figure 5. It is clearly demonstrated that over this time period the longitudinal surface plasmon resonance of silver nanorods shifts to shorter wavelengths and eventually merges with the transverse surface plasmon resonance indicating that spherical nanoparticles have formed. This effect has also been observed in the gold nanorod films. However, the rate at which the longitudinal surface plasmon resonance shifts to shorter wavelengths for the gold nanocomposites is much slower. Over a period of 24 h at 100 °C, the longitudinal surface plasmon resonance shifted from 796 to 630 nm, correlating with a change of 3.5 to just under 2 for the aspect ratio of the rods. Over this time period, the gold nanorods were not able to convert into spheres.

The use of more than one metal for the formation of nanoobjects and their subsequent entrapment in a polymer matrix for use as thermochromic materials open up the possibility of combining nanoobjects of different shape and size in addition to the combination of nanoobjects fabricated from different elements in order to tune the color and temperature at which thermochromic transition occurs. A simple demonstration of this principle is shown in Figure 6. One color that is difficult to obtain using only variation of the size and shape of either gold or silver nanoobjects is green. However, it is relatively easy to produce blue gold nanorods (aspect ratio = 2.0) and spherical yellow silver nanoparticles. By subtractive color mixing of these two different nanoobjects, the color green is obtained. When this new green film is then heated to 200 °C, the blue nanorods change shape, becoming spheres corresponding to a red color. Therefore, the green film after heating is composed of spherical gold (red) and silver (yellow) nanoparticles, giving rise to an orange/red color. The UV spectra of these films, before and after heating, are shown in Figure 6. As can be seen, there are three signals before heating arising from the two plasmonic resonances of the gold nanorods and one from the spherical silver nanoparticles. After heating, there are only two signals corresponding to the single plasmonic resonance of the gold and silver spheres, indicating that the gold nanorods have changed shape whereas the silver nanoparticles have remained unaffected.

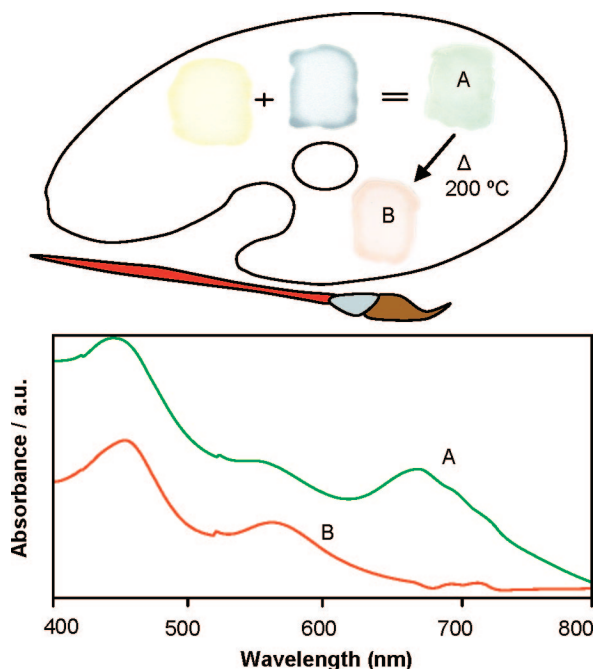


FIGURE 6. Diagram depicting the mixing of gold nanorods (blue) and silver nanoparticles (yellow) in order to obtain the color green and the subsequent heating of this green film (A) to 200 °C to give a thermochromic transition to an orange/red color (B). The UV-vis spectra of the green (A) and orange/red (B) films are also included.

CONCLUSION

In conclusion, irreversible thermochromic behavior has been observed in gold and silver nanorod/PIL nanocomposite films. The thermochromic behavior has been attributed to the distinct color changes associated with the thermally induced variation in the aspect ratio of the nanorods. Altogether, this article opens up new routes in the design of a new generation of irreversible thermochromic nanocomposites. The use of other types of nonspherical metal nanoparticles, based on other metals such as copper or alloys and different polymer matrixes, opens new possibilities to tuning the range of colors and the thermochromic transition temperature. This will allow for the development of innovative thermochromic products with applications such as warnings for perishables foods and pharmaceuticals or sensitive electronic circuitry that may have been exposed to undesirable temperatures.

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