

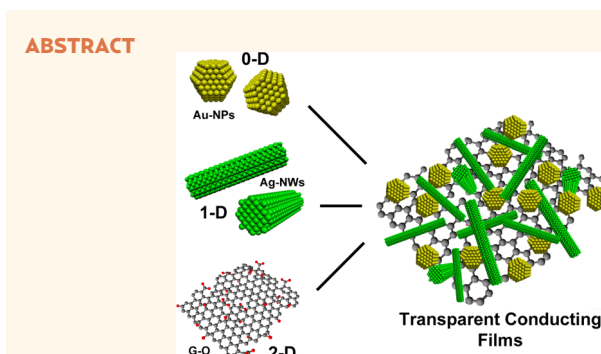
# Hybrid Films with Graphene Oxide and Metal Nanoparticles Could Now Replace Indium Tin Oxide

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The isolation of graphene, an atom-thick layer of  $sp^2$ -hybridized carbon atoms, using repeated peeling (the “scotch tape” method) as first described by Novoselov *et al.*<sup>1</sup> demonstrated that it is indeed possible to obtain atom-thick two-dimensional (2D) materials. Novoselov and co-workers then fabricated the first field-effect transistor (FET) using these 2D carbon sheets, and soon after, numerous groups worldwide uncovered the unprecedented physicochemical properties of graphene, such as high electron mobility, excellent thermal conductivity, integer quantum Hall effect, *etc.*<sup>2,3</sup> The isolation of graphene generated a great impact in the physics and chemistry communities, and the Nobel Prize in Physics was awarded in 2010 to A. Geim and K. Novoselov. The intense activity of graphene research can be confirmed by an exponential increase in the number of publications per year (Figure 1).

The fact that graphene exhibits high electron mobilities and the quantum Hall effect at room temperature suggests the possibility of various applications in electronics, which could eventually replace the current silicon-based electronics. However, further fundamental research is needed in this direction. For example, large-area defect-free graphene surfaces are required for the fabrication of electronic devices, and researchers are now investigating the reproducible synthesis of homogeneous and highly crystalline graphene sheets on non-conducting substrates. In addition to possible electronic applications, graphene could also be used in other fields. It is noteworthy that graphene is the strongest material known,<sup>2,4</sup> which might lead to the fabrication of robust and highly conducting composites.<sup>5,6</sup> Because graphene is also so thin (one atom thick), highly conducting,



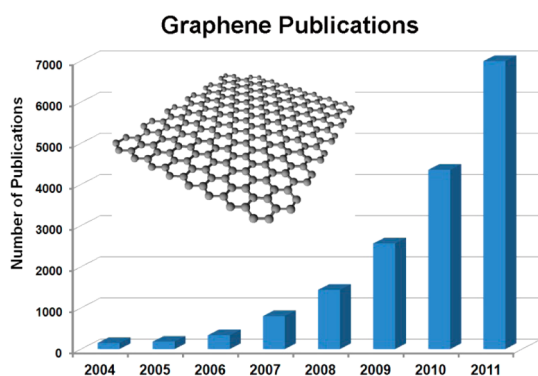
Graphene oxide (G-O), a highly oxidized sheet of  $sp^2$ -hybridized carbon with insulating electrical properties, can be transformed into graphene if it is adequately reduced. In the past, researchers believed that reduced G-O (rG-O) could be highly conducting, but it has been shown that the presence of extended vacancies and defects within rG-O negatively affect its electrical transport. Although these observations indicated that rG-O could not be used in the fabrication of any electronic device, in this issue of *ACS Nano*, Ruoff's group demonstrates that rG-O can indeed be used for producing efficient transparent conducting films (TCFs) if the rG-O material is coupled with Au nanoparticles (Au-NPs) and Ag nanowires (Ag-NWs). The work further demonstrates that these hybrid films containing zero-dimensional (Au-NPs), one-dimensional (Ag-NWs), and two-dimensional (rG-O) elements exhibit high optical transmittance (*e.g.*, 90%) and low sheet resistance (20–30  $\Omega/\square$ ), with values comparable to those of indium tin oxide (ITO) films. In addition, Ruoff's group notes that the presence of Ag-NWs and rG-O in the films showed antibacterial properties, thus demonstrating that it is now possible to produce flexible TCFs with bactericidal functions. The data show that smart hybrid films containing rG-O and different types of NPs and NWs could be synthesized easily and could result in smart films with unprecedented functions and applications.

and transparent, it could be used in optoelectronics.<sup>4</sup> However, some of these applications require the synthesis of kilogram quantities of graphene (*e.g.*, for composites), and alternative methods for such large demand need to be developed. In this context, the synthesis of graphene oxide (G-O) using bulk  $sp^2$ -hybridized carbon sources (*e.g.*, graphite, nanotubes, nanofibers), which

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**Figure 1.** Number of articles published on graphene since 2004 according to the Web of Science. Inset shows the molecular model of a graphene sheet. The number of publications experienced a remarkably fast increase in the last two years, after the Nobel Prize in Physics was awarded to Geim and Novoselov in 2010. The numbers were obtained using the topic keyword “graphene”.

was improved by Boehm in the 1950s,<sup>7,8</sup> was recently modified by Ruoff's group<sup>9</sup> in order to obtain single sheets of G-O. This highly oxidized graphene could then be reduced (to rG-O) using chemical<sup>9–12</sup> or thermal approaches.<sup>13–16</sup> The synthesis of rG-O can easily be scaled up, thus remediating the high demand for the bulk amounts of graphene that are needed for some of the above-mentioned applications. There are similarities among “scotch tape” graphene, chemical vapor deposition (CVD)-grown graphene, and rG-O but also noteworthy differences. Each of these graphene materials has advantages in specific applications, and the quest for the fabrication of novel graphene-based products strongly depends on their specific properties. In evaluating the impact of G-O and rG-O, we can observe that the number of publications on G-O increased dramatically in 2011 (Figure 2), and we expect that the numbers of publications on G-O will increase at a similar rate as that shown for graphene (Figure 1). The field of rG-O is also increasing in number of publications (although not as rapidly as graphene or G-O), and we expect that this area will follow the publication trajectories of graphene and G-O (Figure 2).

In this Perspective, we will summarize the similarities and differences between CVD-grown graphene and reduced graphene oxide (rG-O)

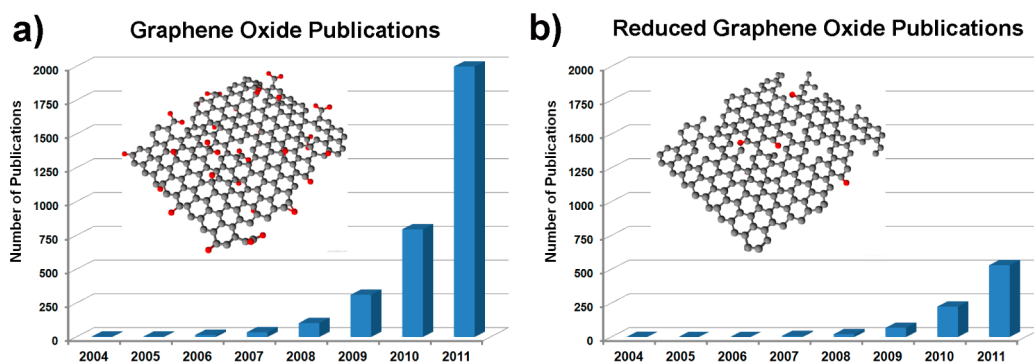
and discuss some of their physico-chemical properties, their synthesis methods and yields, and some of their potential applications. Because G-O is a highly defective (oxygen decorated) graphene layer (Figure 2a inset) that can never be totally converted into defect-free graphene after reduction (Figure 2b inset), rG-O is not suitable for electronic transport applications such as the fabrication of FETs. Soon after the synthesis of G-O was reported,<sup>9</sup> scientists and industrialists believed that rG-O could replace indium tin oxide (ITO) when producing transparent conducting films (TCFs), but unfortunately, rG-O revealed high film resistances with values 2–3 orders of magnitude larger than those obtained for ITO.<sup>16–18</sup> However, in this issue of *ACS Nano*, Kholmanov *et al.*<sup>19</sup> demonstrate that it is indeed possible to use rG-O to construct efficient TCFs if rG-O is used in conjunction with Au nanoparticles (Au-NPs) and Ag nanowires (Ag-NWs). The new hybrid films containing zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D) components, Au-NPs, Ag-NWs, and rG-O, respectively, exhibit values comparable to ITO-based TCFs. These results open up new avenues to exploit rG-O materials in the fabrication of flexible TCFs that are not possible when using ITO. The current high price of indium makes the above-mentioned rGO-based alternative viable. Therefore, it is expected

that various industries will start to improve the functions of hybrid films in order to make competitive TCFs based on rG-O, at lower costs than the comparable ITO-based TCFs.

In this issue of *ACS Nano*, Kholmanov *et al.* demonstrate that it is indeed possible to use reduced graphene oxide to construct efficient transparent conducting films if reduced graphene oxide is used in conjunction with Au nanoparticles and Ag nanowires.

It is also noteworthy that Ag-NPs and NWs are commonly used as antibacterial materials, and these hybrid TCFs could also be used to bactericidal advantage in touch screens that are in contact with numerous persons each day; ITO does not offer this possibility. It is therefore clear that the synthesis of hybrid films based on rG-O, NPs, and NWs constitutes the beginning of a new field, and smart films with other functionalities based on rG-O can now be developed and investigated.

**Graphene and Graphene Oxide.** Graphene, which consists of a perfect (defect-free) hexagonal network of  $sp^2$ -hybridized carbon atoms (Figure 1 inset), exhibits fascinating electronic and mechanical properties. Films consisting of highly crystalline graphene can be synthesized in minute amounts by (i) the thermal decomposition of hexagonal SiC at elevated temperatures ( $>1200$  °C),<sup>20</sup> (ii) mechanical/ultrasonic exfoliation of graphite,<sup>21</sup> or (iii) methane CVD over Cu<sup>22</sup> or Ni foils.<sup>23</sup> The drawbacks of using CVD-grown graphene or



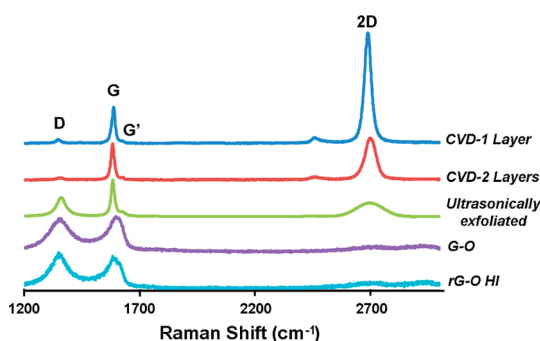
**Figure 2.** Number of articles published since 2004 on (a) graphene oxide (G-O) and (b) reduced G-O (rG-O). The data were obtained from the Web of Science. After the 2010 Nobel Prize in Physics, the G-O publication rate shot up. The rG-O area is growing at a slower pace, but it is expected to increase as rG-O is used in different applications related to composites, transparent conducting films, etc. The data were obtained using the topic keywords “graphene AND oxide”, and “reduced AND graphene AND oxide”. Insets show molecular models of G-O (a) and rG-O (b).

thermally annealed SiC graphene include the expensive costs associated with the high-temperature processes (e.g., 950 °C for CVD graphene or >1200 °C for SiC-based graphene). In addition, for CVD-grown graphene, chemical methods need to be used to transfer the graphene sheets from metallic substrates to nonconducting substrates. Mechanical exfoliation has disadvantages, as well, such as the complicated separation through centrifugation–decantation cycles, the restacking tendency of the isolated sheets, and the challenging purification of the large sheets. For applications that require kilogram or even ton quantities of graphene (e.g., composites), the methods described above are not suitable because they are only capable of yielding small quantities of graphene. However, G-O and rG-O could be produced in gram and even kilogram quantities. Unfortunately, rG-O possesses a highly defective structure with extended vacancies that are created by the liberation of the majority of oxygen atoms (see Figure 2b inset), and these defects result in much lower electrical conductivity values when compared to perfect (defect-free) graphene.

The preparation of G-O has evolved over the last century and a half; it was first reported in 1859 and was followed by two alternative synthetic routes described in 1898 and 1958.<sup>24</sup> Graphite oxide, or GO (*no hyphen*), was first obtained by

the decomposition of unstable graphite intercalated compounds (GIC) with acids and oxysalts (H<sub>2</sub>SO<sub>4</sub>, NaNO<sub>3</sub>, and KMnO<sub>4</sub>), which resulted in graphite with multiple oxygen complexes and functional groups in which the layers increased their interspacing by a factor of 3. Graphite oxide can be defined as a nonstoichiometric compound, in which the carbon layers are separated, corrugated, and decorated with oxygen complexes. In addition, it is electrically insulating, and the precise chemical structure is uncertain and remains a topic of debate. Following the isolation of graphene in 2004, GO was thought to be a precursor able to detach individual layers of graphene oxide (G-O) after exfoliation by sonication. Graphene oxide consists of individual platelets of highly oxidized monolayer graphene (see Figure 2a inset) that are stable in different solvents. These individual layers of G-O consist of a graphene sheet bonded to epoxide, hydroxyl, carbonyl, and carboxyl groups from both sides of the basal planes and at its edges (see Figure 2a inset). As mentioned above, G-O is easy to synthesize, and the process could be scaled up to produce grams or kilograms per day. Ruoff and co-workers<sup>9</sup> were the first to report the chemical reduction of G-O using hydrazine and observed that the material enhanced the electrical conductivity of rG-O but never reached the high electrical con-

ductivity of pristine (defect-free) graphene. Subsequently, Becerril *et al.*<sup>18</sup> reported the hydrazine reduction process of substrates coated with G-O. These experiments yielded transparent films with surface resistivities only 1 order of magnitude larger than ITO. This reduced G-O was initially mislabeled graphene, or functionalized graphene, causing confusion when differentiating it with highly crystalline graphene. Although rG-O exhibits significantly enhanced electrical conductivity, it never reaches the conductivity of defect-free graphene because some oxygenated groups remain on its surface (see Figure 2b inset), in addition to the presence of extended vacancies. This fact can be observed *via* the intensity of the 2D-band in the Raman spectroscopy data. For perfect crystalline single-layer graphene, the intensity of the 2D-band (double resonance peak characteristic of graphitic materials and located at *ca.* 2650 cm<sup>-1</sup>) is double the intensity of the G-band (a Raman signal coming from the tangential modes of the perfect hexagonal carbon network with signal at *ca.* 1600 cm<sup>-1</sup>).<sup>25,26</sup> As the number of layers increases, the intensity and full width at half-maximum (fwhm) of the 2D peak decreases and widens, respectively (Figure 3).<sup>25</sup> If the degree of crystallinity of graphene or few-layered graphene is reduced, the Raman



**Figure 3.** Raman spectra corresponding to different types of graphene-related materials in which the D-, G-, G'-, and 2D-bands appear. Defect-free single-layer (atom-thick) graphene exhibits the largest band intensity ratio for  $I_{2D}/I_G$  (ca. 2), whereas other types of graphene, such as ultrasonically sonicated graphite, G-O, and rG-O, reveal much lower  $I_{2D}/I_G$  values, indicating that the latter forms of graphene are less crystalline and do not necessarily consist of atom-thick layers.

spectrum will show the presence of the D-band located at ca.  $1325\text{ cm}^{-1}$ . Therefore, by studying the intensity ratios of the D-, G-, and 2D-bands, one can determine the number of graphene layers and the degree of crystallinity of samples (Figure 3). For example, it has been observed that, with ultrasonically exfoliated graphite, the 2D-band decreases significantly in intensity and broadens;  $I_{2D}/I_G \approx 0.5$  (see Figure 3). These values are due to the presence of less crystalline material, possibly due to the introduction of oxygen groups in addition to structural defects within the hexagonal lattice (extended vacancies, edges, etc.). For a high-quality reduced monolayer of G-O (rG-O), the 2D-band is even lower in intensity ( $I_{2D}/I_G \approx 0.15$ ), indicating that rG-O still has defects such as oxygen groups and could be stacked with other layers (see Figure 3). Therefore, the electrical transport of rG-O will not approach the values observed for perfect single-layer graphene.

However, rG-O still offers many advantages when compared to pure and crystalline graphene: (i) it can be produced in high yields; (ii) it can consist of a monolayer sheet if it is sufficiently reduced (this is an advantage in the fabrication of transparent films); (iii) the residual oxygen groups could be advantageous for forming stable suspensions with solvents, monomers, polymers, biomolecules, etc.; and (iv) uniform

and stable dispersions of rG-O in solvents could be useful in nanocomposite fabrication (this does not occur with graphene grown by CVD on metallic substrates or SiC-derived graphene).

**Synthetic Methods for Producing G-O and rG-O.** The most common source used to produce G-O has been graphite. However, other types of  $sp^2$ -like hybridized carbon such as carbon nanotubes and carbon nanofibers could be used as the starting material to generate G-O. In particular, the unzipping of carbon nanotubes using a modified Hummers method reported by Tour's group<sup>27–29</sup> provided a high yield of G-O nanoribbons, and a similar reaction could be used to unzip (exfoliate) carbon nanofibers.<sup>30,31</sup>

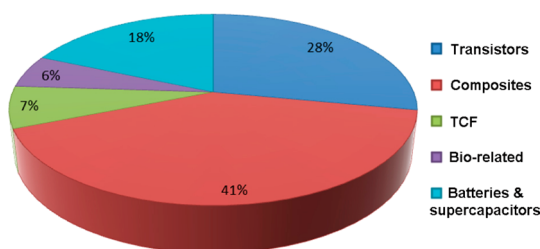
Once G-O is synthesized, it can be reduced in order to remove the large number of oxygen groups anchored to its surface and thus signifi-

cantly enhance its electrical conductivity. In this context, there are several reduction strategies that include the thermal treatment in various atmospheres and chemical routes.

When carrying out thermal annealing, the temperature, heating rate, and reducing atmosphere (inert, reducing, or vacuum) are key parameters to be controlled. High temperatures ( $>700\text{ }^\circ\text{C}$ ) are usually used in order to achieve high C/O ratios; the presence of oxygen is avoided by having an excellent vacuum or by adding a reducing gas such as  $\text{H}_2$  during annealing.<sup>13</sup> If the thermal reduction occurs under a low pressure of ammonia ( $\text{NH}_3$ ), the G-O sample can be simultaneously reduced and doped with N.<sup>32</sup> Upon annealing, the heating rate should be slow enough to prevent an abrupt expansion, which results in the formation of small rG-O pieces containing a large number of defects and extended vacancies that negatively affect the electronic properties of the material. In addition to the thermal heat treatments, G-O can be reduced *via* microwave irradiation<sup>33</sup> and photoirradiation using a xenon lamp.<sup>34</sup>

The chemical reduction of G-O can take place in the presence of hydrazine and metal hydrides (sodium hydride, sodium borohydride, and lithium aluminum hydride) but cannot be used in water solutions of G-O.<sup>11</sup> Alternatively, ascorbic acid (vitamin C) could be considered to be a green alternative for reducing G-O.<sup>35</sup> More recently, hydrogen iodide (HI) has emerged as an efficient reducing agent that can form stable colloids of rG-O that can then lead to powders or films. Recently, it has been demonstrated that G-O films reduced with HI retain good mechanical flexibility and have improved tensile strength, whereas films reduced using hydrazine become rigid and introduce nitrogenated groups that affect the electrical conductivity.<sup>11</sup> For this reason, HI treatments have attracted the attention of numerous researchers who use this

Once graphene oxide is synthesized, it can be reduced in order to remove the large number of oxygen groups anchored to its surface and thus significantly enhance its electrical conductivity.



**Figure 4.** Distribution of publications related to applications of graphene-like materials. Composites and transistors dominate with more than 50% of publications, whereas publications on TCF applications correspond to 7%.

method when reducing G-O films for TCF applications.<sup>17,36</sup>

Electrochemical reduction<sup>37</sup> and photocatalyst reactions,<sup>38</sup> in conjunction with a photocatalyst such as TiO<sub>2</sub>, have been recently reported as alternatives for reducing G-O. Other methods involving solvothermal reduction in sealed containers in the presence of a solvent above its boiling point have been successfully used to reduce G-O.<sup>39</sup> Similarly, overheated supercritical water has been used to replace organic solvents.<sup>40</sup>

From the above discussion, it is clear that there is not an optimal method to reduce G-O, and current strategies should combine some of the methods described. The simplest method consists of a chemical reduction followed by thermal annealing.<sup>18</sup> Other more sophisticated methods include a dehydration step with sulfuric acid before thermal annealing.<sup>41</sup>

The main objective when reducing G-O is the formation of a graphene-like material with an increased C/O ratio, but unfortunately, these reduction methods result in the creation of structural defects within the sheets that reduce significantly their electrical conductivity, which is detrimental if these rG-O films are to be used in the fabrication of TCFs, for which high transparency and high electrical conductivity are desirable. Researchers have tested different approaches with the aim of improving the electrical transport of rG-O. For example, rG-O films can be exposed to a carbon source (under conditions similar to those used for CVD).<sup>42</sup> This strategy results in a decrease of the sheet resistance by an order of magnitude.<sup>42</sup> Another alternative is to fabricate

hybrid films using conducting particles.<sup>43</sup> This route, consisting of intercalating layers of G-O with different types of metallic nanoparticles or nanowires, opens up the possibility of fabricating smart films that could exhibit high transparency, enhanced electrical conductivity, and good flexibility, in addition to enabling attractive biological applications, as reported by Ruoff's group in this issue of *ACS Nano*.<sup>19</sup>

**Possible Applications of G-O and rG-O.** Regarding applications of graphene-like materials, it is noteworthy that the largest number of publications is devoted to composites, followed by transistors and energy harvesting (Figure 4). Transparent conducting films and biological applications are not as popular as the above-mentioned applications, but we expect that the work of Kholmanov *et al.*<sup>19</sup> will spark more investigations in these areas.

We expect that the work of Kholmanov *et al.* reported in this issue of *ACS Nano* will spark more investigations in the areas of transparent conducting films and biological applications.

**Reduced G-O for Transparent Conducting Films.** Some authors have reported that rG-O films can exhibit sheet resistances (840 Ω/□ at a transmittance of 78%)

comparable to those obtained for graphene films grown on Ni substrates.<sup>17</sup> However, the contribution of Ruoff's group<sup>19</sup> now demonstrates that TCFs with sheet resistances of 20–80 Ω/□ at transmittances of ca. 80% can be obtained by fabricating hybrid films consisting of rG-O, metal clusters, and metal nanowires.<sup>19</sup> These hybrid systems take advantage of the components Au-NPs (0D), Ag-NWs (1D), and 2D rG-O (2D) and result in TCFs with values comparable to those obtained for ITO (Figure 5).<sup>19</sup> In this case, the defective surface of rG-O is advantageous because the defects act as nucleation sites able to anchor Au-NPs efficiently.

The electrical conductivity of the Ag-NW films is a consequence of the formation of a percolation network of NWs that strongly depends on the NW concentration. The high optical transparency is also provided by the open spaces between Ag-NWs. In Ruoff's work,<sup>19</sup> films of Ag-NWs, prepared by spin coating using dispersions of different concentrations (1.0, 2.0, and 2.5 mg/mL), were compared in terms of conductivity and transmittance. The dispersion of lower concentration provided a film with a transmittance of  $T_{550} = 96\%$  but was not conductive because percolation of the NWs was not achieved. The films with Ag-NW concentrations of 2.0 and 2.5 mg/mL exhibited transmittances of 90 and 88% and sheet resistances of 740 and 520 Ω/□, respectively.

Reduced G-O films are continuous, but their electrical conductivity is inhibited by the presence of defects and the interlayer resistance between platelets. Therefore, at high transparency (94%), a sheet resistance of ca. 50 kΩ/□ is expected for rG-O films.<sup>16,19</sup> In order to improve the electrical conductivity using rG-O, Kholmanov *et al.*<sup>19</sup> combined rG-O with Au-NPs and Ag-NWs. A small amount of Au-NPs increases the conductivity of the rG-O platelets and does not affect the transparency. The resulting rG-O/Au-NP films revealed sheet resistances of 28.6 kΩ/□.

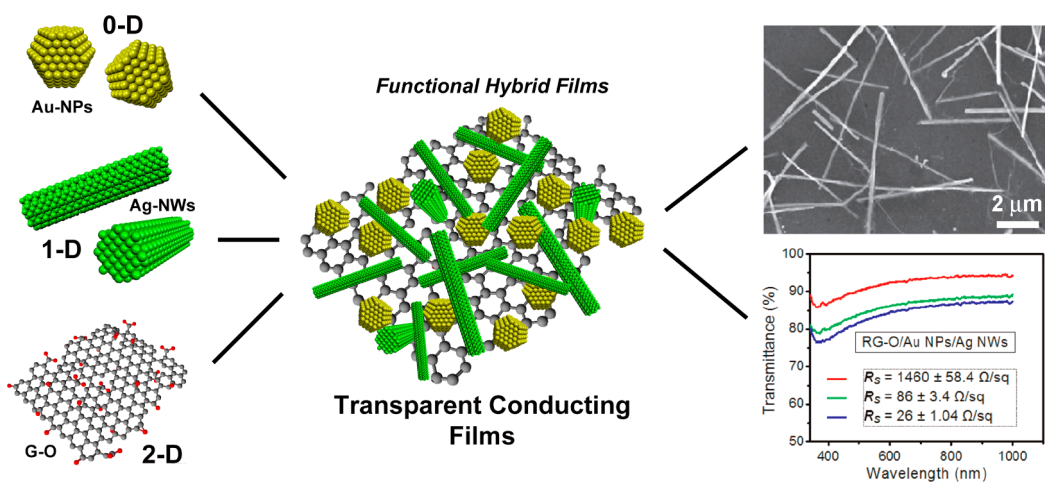


Figure 5. Schematic representation showing the composition of the hybrid films reported by Ruoff's group.<sup>19</sup> The films are produced by assembling G-O/Au-NPs and Ag-NWs. The films exhibit reduced electrical sheet resistances (e.g.,  $26 \Omega/\square$ ) and high transparencies (e.g., 83%) that are comparable to the values obtained for ITO. SEM image of the films and transmittance plots correspond to the data reported in ref 19.

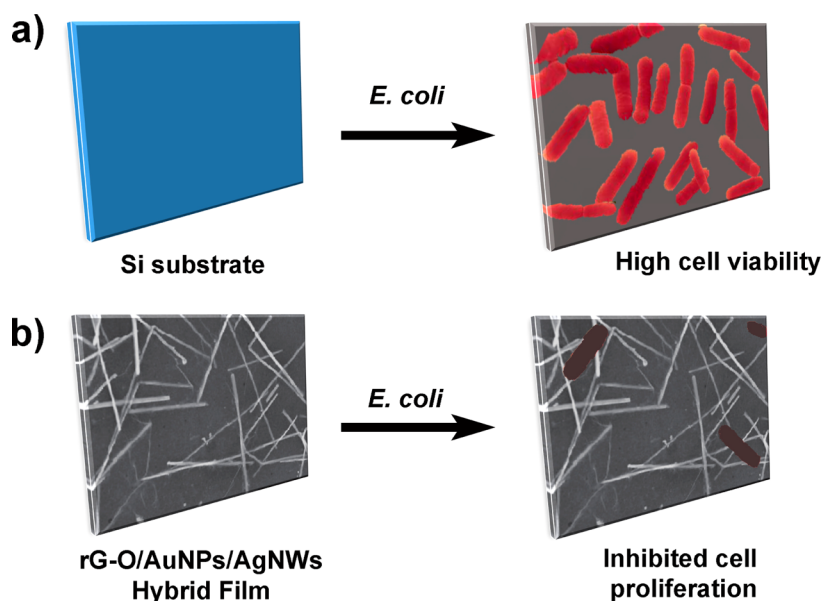


Figure 6. Schematic of the bactericidal effect of the hybrid films reported by Kholmanov *et al.*<sup>19</sup> in comparison with control experiments on Si wafers: (a) control experiments on Si, in which *E. coli* easily replicate and exhibit high cell viabilities; (b) *E. coli* do not adhere to the hybrid films (rG-O/Au-NPs/Ag-NWs) due to the presence of Ag-NWs and rG-O, and the films efficiently kill bacteria by destroying the outer cell membrane of *E. coli*. SEM image of hybrid film reproduced from ref 19. Copyright 2012 American Chemical Society. For clarity, killed bacteria are represented in dark gray, whereas live bacteria are depicted in red. Note that these images are schematic representations and do not correspond to the experiments carried out by Kholmanov *et al.*;<sup>19</sup> they are intended to explain the results.

The subsequent addition of Ag-NWs minimizes the junction resistance between rG-O platelets, even at sub-percolation concentrations, thus resulting in a sheet resistance of  $26 \Omega/\square$  at  $T_{550} = 83\%$ . The schematic preparation of these films is shown in Figure 5. First, a Ag-NW solution is spin coated on the substrate, then covered by a solution of G-O/Au-NPs, also by spin coating, and the

hybrid film is then reduced with hydrazine vapor.<sup>19</sup> The contact between Ag-NWs and rG-O enhances the charge transfer between these two components, thus resulting in increased electrical conductivity. It is noteworthy that Ag-NWs are quite reactive to species present in the environment such as  $H_2S$ , and this reactivity could lead to significant decreases in electrical transport.

Since G-O is inert to these reactive species present in air, by covering Ag-NWs with G-O, one could prevent electrical degradation of the Ag-NWs.<sup>44</sup>

Interestingly, the Ag-NWs within these hybrid films prepared by Ruoff's group<sup>19</sup> display a clear bactericidal effect, which is also enhanced by the presence of rG-O.<sup>45</sup> The bactericidal properties were

investigated after carrying out two experiments: the first consisted of the ability of bacteria (*Escherichia coli*) to attach to the film surface in solution experiments; the second was related to the growth of bacterial colonies (*E. coli*) from solutions sprayed on the hybrid films. As a consequence of the bactericidal properties of the hybrid films, *E. coli* did not adhere to the hybrid films and no bacteria were monitored in the viability experiments. The presence of Ag-NWs and rG-O destroyed the outer cell membrane of *E. coli* and inhibited their proliferation (see Figure 6).

Therefore, these films are multifunctional and could be used as TCFs with bactericidal activity, which might be particularly useful for electronic applications in medical or public environments. The concept of multifunctional or “smart” films using rG-O in conjunction with other nanoparticles (*e.g.*, luminescent, ferromagnetic, catalytic, *etc.*) and 1D systems (ZnO, Fe, BN, MoS<sub>2</sub>, *etc.*) could result in fascinating materials with endless possibilities of applications, and further experimental work in the areas of physics, chemistry, biology, toxicology, materials science, and engineering needs to be conducted.

**Conflict of Interest:** The authors declare no competing financial interest.

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