Graphene oxide - potential use in wood protection based on a review of antibacterial and fungicide properties

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Abstract: Graphene oxide - potential use in wood protection based on a review of antibacterial and fungicide properties. Graphene oxide is a material that has been generating interest among researchers in recent years. Due to its properties, it can be used in many scientific and industrial fields. Not all of its properties are significantly known, making it a potential subject of research in many different aspects. The topic of this article is to assess the potential applications of graphene oxide in the field of wood science industry. Based on the literature, the antibacterial and fungicidal properties are characterised. The fungicidal effect of graphene oxide, mainly in plant protection, leads to consideration of the potential use of this material in protection against wood-destroying fungi.

Keywords: graphene oxide, fungicides, wood protection

INTRODUCTION

Recent years have seen a high level of interest in graphene-based materials in various scientific fields. There are an increasing number of publications reporting research results using graphene (G) and its derivatives - graphite, graphite oxide, graphene oxide (GO) and reduced graphene oxide (rGO). The high potential of this group of materials is due to a number of diverse properties, thus giving them a wide range of application possibilities. Research results, concerning antibacterial and fungicidal properties in the area of, among other things, plant protection, are promising in terms of efficacy. However, there are few reports from the field of forest sciences on the effect of graphene oxide on the growth of wood-destroying fungi. However, there are indications to consider the usefulness of using graphene oxide as an agent for destroying fungal growth in wood.

GRAPHENE OXIDE - BASIC INFORMATION

Graphene oxide is a material that is created by a two-step process. The starting material is graphite, which undergoes an oxidation process. The graphite oxide formed in this process undergoes intercalation in a further step, whereby it is transformed into graphene oxide (GO). One of the first researchers to make observations on graphite was the British chemist Benjamin Collins Brodie [1859]. He conducted research using graphite powder in combination with potassium chlorate (KClO₃) in fuming concentrated nitric acid (HNO₃).
During the reaction, he obtained carbon, hydrogen and oxygen - the latter reaching a maximum value after a series of experiments. He established that there was an increase in the mass of graphite during the reaction. His experiments were not precise enough to determine the exact mass of graphite obtained, however, he did obtain a way to oxidise graphite. Another method was developed by the German scientist Staudenmaier [1898], who introduced a modification of Brodie’s method by using smaller batches of potassium chlorate (KClO3) and a stronger acidic environment, adding concentrated sulphuric acid (H2SO4). This action allowed the process to proceed continuously, eliminating the replenishment of the evaporating nitric acid [Ciszewski and Mianowski 2013]. Subsequently, Hummers and Offeman [1958] proposed a method of oxidising graphite using the reaction of graphite with potassium permanganate (KMnO4) in an environment of concentrated sulphuric acid (H2SO4). This experiment allowed a significant reduction in the oxidation reaction time, making it the most widely used method for obtaining graphite oxide. In addition, the relatively low production costs and efficiency of the process influence the industrial use of this method. Graphite oxide obtained by oxidation undergoes intercalation, i.e. expansion, which increases the distance between graphene planes [Smędowski and Muzyka 2013]. This process results in the separation (exfoliation) of graphite layers into individual sheets. The end result is the obtaining of graphene oxide. This material, as a result of the processes taking place, changes the hybridisation of carbon atoms from sp2 to sp3 and is enriched with functional groups containing oxygen atoms, such as hydroxyl (-OH), epoxy (-O-), carbonyl (-C=O) and carboxyl (-COOH) groups.
Graphene oxide is widely used in many scientific fields as a material with distinctive properties and numerous possibilities for their modification. Due to its lower production costs and simpler production process compared to graphene itself while having equally attractive properties, it is constantly being considered for new applications. Due to its very good adsorption properties, graphene oxide is used for the production of gas sensors [Yabaş et al. 2023, Kang et al. 2023], humidity sensors [Guo et al. 2022, Liang et al. 2023] or biosensors [Lee et al. 2016, Singh et al. 2022]. The ability to functionalise the graphene oxide surface provides ample opportunities to obtain more selective sensors. Both gas sensors and humidity sensors take advantage of the presence of functional groups that, by combining with gases or water, influence the conductivity parameters of graphene oxide. The optical properties of graphene oxide can also be important in the design of biosensors [Ikram et al. 2023, Porro et al. 2016].

The adsorption properties also make graphene oxide suitable for use as a filter material. Membranes based on graphene materials are used for water purification [Xu et al. 2013] or gas separation [Park et al. 2016]. However, it is important to take into account studies on the adverse effects of graphene oxide on living organisms and the environment [Ou et al. 2016, Ghulam et al. 2022].

Graphene oxide, after a reduction process, acquires electrical properties similar to those of graphene so that it can be used to produce electronic components such as: transistors, memristors or transparent conductive films [Sundaram 2014]. This is supported by the monolayer thin structure of the material, stability of parameters, flexibility, ease of application, and the possibility of modifying conductive properties. It is also possible to use graphene oxide for the production of capacitors [Rashi 2023], or batteries characterised by small size, high capacity and fast charging and long life [Aleksandrzak and Mijowska 2015].

The exceptional properties, including strength properties, of graphene oxide justify its use in the production of modern composites or nanocomposites. The addition of graphene oxide can positively influence the strength parameters of materials such as cement [Wang et al. 2015], chitosan-based nanocomposites [Yang et al. 2010] or glass fibre composites with epoxy resin [Mannov et al. 2013]. Additionally, the coatings themselves obtained using graphene oxide, in addition to an increase in strength, can gain characteristics such as an increase in resistance to water, alcohols [Xu et al. 2022] or corrosion [Hussain et al. 2019].

In medicine, graphene oxide is used in addition to the previously mentioned biosensors also as a wound dressing material or drug carrier [Patil et al. 2021, Sun et al. 2008]. Graphene oxide itself already exhibits antibacterial properties [Hu et al. 2010], and it is possible to extend these properties by producing nanocomposites based on it with appropriate particles or compounds, e.g.: silver [Kędziora et al. 2013, Wang et al. 2023], silicon [Dan et al. 2023] or iron [Tian et al. 2014]. Graphene oxide also performs well as a drug carrier due to its large adsorption surface area [Sahu et al. 2020]. Nevertheless, there has been a study showing negative effects of graphene oxide on the human body [Zhang et al. 2011] so it is important to continue research and seek solutions to reduce these negative effects.

In addition to its antibacterial properties, graphene oxide also exhibits fungicidal [Zhang et al. 2022, Peng et al. 2022] and insecticidal properties [Wang et al. 2019]. Additionally, there have been studies on the effects of graphene oxide on plant growth [Park et al. 2020] or on increasing plant resistance to drought conditions [Zhao et al. 2022]. Studies on the effects of graphene oxide on plants show both negative and positive effects depending on a number of factors [Yang et al. 2022]. At the same time, the previously indicated antibacterial, fungicidal and insecticidal properties demonstrate the potential
for wider use of graphene oxide-based compounds in plant protection. In addition to the use of graphene oxide itself and graphene oxide-based nanoparticles, it may also be possible to use it as a carrier for pesticides to enhance their effects [Wang et al. 2019].

The attractiveness of graphene oxide is due to its individual set of properties and the possibility to modify them. The material is used in a wide range of scientific fields, whether engineering, science or agriculture. The versatility and wide range of applications of this material shows that it is reasonable to explore the possibility of using graphene oxide in woodworking. The use of graphene oxide in the woodworking industry, as a component of fractions, as a modifier of paint and varnish coatings or binders, but also in wood protection should be considered.

**GRAPHENE OXIDE - FUNGICIDE AND ANTIBACTERIAL PROPERTIES**

Graphene oxide, which is a graphene derivative, manifests fungicidal properties against certain fungi. Studies also show that graphene oxide synergistically supports selected fungicides. In plant protection fungicide research, a relationship was noted between graphene oxide and protective agents (Mancozeb, Cyproconazole and Difenoconazole) in the control of the fungus *Fusarium graminearum*. The combination of these two substances showed a greater inhibitory effect on mycelial growth than the action of fungicides alone [Wang et al. 2021].

Graphene oxide also has antibacterial properties. Research in this area was conducted by scientists from the Chinese Academy of Sciences, who published the results of their study in 2010 [Hu et al. 2010]. This concerned the use of graphene oxide (GO) and reduced graphene oxide (rGO) as a deleterious agent against selected mammalian cells and *E. coli* bacteria. The study using graphene oxide showed an anti-bacterial ratio against *E. coli* bacteria and achieved better results compared to reduced graphene oxide, which, according to the study authors, is due to the presence of oxygen groups in the GO structure. The same researchers showed that graphene oxide effectively inhibited the growth of *E. coli* by 98.5% [Hu et al. 2010]. The antibacterial properties of graphene oxide against *E. coli* bacteria were also addressed by a group of researchers led by Karthikeyan Krishnamoorthy in 2012 [Krishnamoorthy et al. 2012]. In their study, they used GO carbon nanotubes against gram-negative bacteria *Escherichia coli* (DH5) and gram-positive bacteria *Streptococcus iniae*. In both cases, the antibacterial effect on microbial growth was confirmed, which may confirm the usefulness of this agent in the development of future nanomedicine. In 2011, Shaobin Liu and a group of researchers described the antibacterial effect of graphene-based materials, including graphene oxide, against *Escherichia coli* [Liu et al. 2011]. In addition, the researchers indicated that GO had the highest antibacterial activity among the materials tested (graphite Gt, graphite oxide GtO, graphene oxide GO and reduced graphene oxide rGO). Using scanning electron microscopy SEM, graphene oxide structures, due to contact with its sharp edge, were shown to have a direct effect on the bacterial cell membrane and cause disruption of its continuity [Akhavan and Ghaderi 2010]. Confirmation of the antibacterial effect of graphene oxide on *Escherichia coli* bacteria is possible through the use of methods including spectroscopic methods, transmission electron microscopy, X-ray microscopy, among others. The ultimate death of bacterial cells is demonstrated through the mechanism of cell membrane destruction by graphene and its derivatives, including graphene oxide [Aditya et al. 2018]. The effect of graphene oxide on bacteria was also analysed by researchers led by Juanni Chen in 2013 [Chen et al. 2013]. Two bacteria were used in the study: *P. syringae* and *X. campestris pv. undulosa*. Destruction of almost 90% of the bacteria was observed. The mechanism was based on mechanical damage to the cell membrane. The effect of graphene oxide on microorganisms depends largely on
the quality of the material used, by which is meant its purity, quality, size of structure, chemical structure and applied dose [Romiszewska and Bombalska 2019].

GRAPHENE OXIDE - STATUS OF RESEARCH IN WOOD PRESERVATION AND POTENTIAL APPLICATION IN THE WOOD SCIENCE INDUSTRY

Due to its manifested fungicidal and antibacterial properties, graphene oxide may play an important role against wood-destroying fungi. The previously mentioned 2013 study [Chen et al. 2013] also looked at the effect of graphene oxide against the phytopathogens *F. graminearum* and *F. gypseorum*. The results showed a similar mechanism of fungal cell destruction to that of bacteria. Graphene oxide is a material used in research against wood-destroying fungi. The results, conducted on mould fungi (*Aspergillus niger*), show a clear negative effect of GO, manifested as a change in the structure of the filaments and a reduction in fungal mass [Nguyen et al. 2019]. The effects of graphene oxide (GO) and reduced graphene oxide (rGO) on fungi causing white decomposition are also currently the focus of research [Yang et al. 2018, Xie et al. 2016]. In one of these, one of the fungi responsible for white decomposition, which is *Phanerochaete chrysosporium*, was analysed. It was shown that the growth mechanism was inhibited by a high concentration of applied graphene oxide [Xie et al. 2016]. However, the still small number of publications on fungi developing on wood results in too few references in the literature.

Graphene oxide can also be used in other aspects of wood science industry. Research results are known, indicating an increase in the chemical resistance of composites and an improvement in mechanical strength, due to the introduction of graphene oxide [Krzemińska 2015]. These composites, which are layered aluminosilicates, are characterised by a lamellar structure, thus creating a protective barrier effect [Mikula and Łach 2012]. This effect can be used to support anti-corrosion pigments in metal protection paints, e.g. in furniture fittings. Increased corrosion resistance through the addition of graphene oxide (GO) and reduced graphene oxide (rGO) is also used for water-based acrylic resins used in the furniture industry. In addition, lacquer coatings containing 0.1% GO and rGO do not have cracks and do not peel [Wojucki et al. 2018]. Potential for the use of graphene oxide in the furniture industry are polyelectrolyte films with embedded graphene oxide plates [Kruk 2012]. They are used as a surface modifier by, among other things, changing wettability and imparting greater hydrophilicity. This property can be considered for the application of graphene oxide polymer films for surface finishing of wood-based boards.

CONCLUSION

Based on analyses from both a review of properties and applications, it can be concluded that graphene oxide (GO) can potentially be used in wood protection. Few reports in this area indicate that this is a fledgling development. It is presumed that graphene oxide may exhibit fungicidal properties against fungi that cause wood decay.

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Streszczenie: Tlenek grafenu – potencjalne wykorzystanie w ochronie drewna na podstawie przeglądu właściwości antybakterjnych i fungicydowych. Tlenek grafenu jest materiałem, który w ostatnich latach budzi zainteresowanie wśród badaczy. Ze względu na swoje właściwości może być wykorzystywany w wielu dziedzinach nauki i przemysłu. Nie wszystkie jego właściwości są istotnie poznane, przez co może stanowić on przedmiot badań w wielu różnych aspektach. Tematem tego artykułu jest ocena możliwości potencjalnych zastosowań tlenku grafenu w dziedzinie drzewnictwa. Na podstawie literatury przedmiotu dokonano charakterystyki właściwości antybakterjnych i fungicydowych. Fungicydowe oddziaływanie tlenku grafenu, głównie w ochronie roślin, prowadzi do rozważań nad potencjalnym zastosowaniem tego materiału w ochronie przed grzybami, powodującymi destrukcję drewna.

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