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Nano Marvels: Unleashing Precision with Metal-Oxide/ Reduced Graphene Oxide Synergy in Gas Sensors

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ABSTRACT

Reduced graphene oxide is a modified form of graphene oxide used for gas sensing due to its large surface area and exceptional electrical conductivity. It is suitable for detecting various gases, including carbon dioxide, nitrogen dioxide, ammonia, ethanol and volatile organic compounds. Graphene-based materials have shown promise in gas sensing due to their sensitivity, selectivity, and cost effectiveness. Graphene-based sensors are versatile and can be easily integrated into existing systems, making them suitable for various industrial applications. The adjustable characteristics of graphene enable customization and modification of sensor performance, expanding its potential in gas sensing technology. The main goal of this study is to make metal oxide nanomaterials and reduced graphene oxide using a straight forward chemical method. Samples will be analyzed using X-ray diffraction, Raman spectroscopy, scanning electron microscopy, UV-vis spectroscopy, and X-ray photoelectron spectroscopy. The research aims to assess the performance and efficacy of these nanocomposites compared to other materials in energy storage, catalysis, and sensing applications. The study also explores the parameters affecting gas detection abilities, surface chemistry, and electrical interactions.

Key words: *Reduced graphene oxide, Gas detection applications, Analytical techniques, Gas sensors.*

Introduction

Nanotechnology has revolutionized various fields, including healthcare, electronics, and energy. It involves the control and manipulation of matter at atomic and molecular scales, allowing scientists to create materials with unique characteristics and applications. Graphene, a nanomaterial composed of a single layer of carbon atoms arranged in a hexagonal configuration, is the thinnest and most durable material known. Its remarkable electrical conductivity and flexibility make it suitable for various applications, including electronics, sensors, and energy storage (Anasori, *et al*., 2015).

Gas sensors are fast becoming an imperative part of modern life with extensive applications in domestic safety, greenhouse gas monitoring for environmental studies, industrial process control such as methane detection in mines, in automotive industry for evaluating the exhaust of cars for pollution control check, public security, medical applications such as electronic noses simulating human olfactory system and chemical warfare assessment. They are being progressively employed in mass-market applications, such as in indoor air quality control as well as the more conventional areas of explosive and toxic gas detection. An efficient gas sensing technique is characterized by certain performance parameters such as: (i) High sensitivity (ii) Low detection limit i.e. the minimum volume of target gas concentration at which response is generated should be low (iii) Good selectivity which means that the sensor should be able to detect a particular gas from a given gas mixture (iv) Faster response time (v) Short recovery time (vi) Operating Temperature should be ambient (vii) Reversibility i.e. the sensing material should return to its original state after detection is complete (viii) Good Adsorptive capacity (ix) Low Fabrication cost (x) Stability of Operation (Gupta and Ravikant, 2018).

Conventional gas sensors often employ polymers or metal-oxide semiconductors as active materials. These sensors utilize many techniques for sensing, including calorimetric, optoelectronic, gas chromatography, mass spectrometry, and acoustic approaches. These methods are usually very costly with high power consumption, bulky devices and poor miniaturization due to which they are limited for real-time use. Also, for practical use, the sensors need to be thermally stable and their operation should not be significantly affected by ambient conditions (Gupta and Ravikant, 2018).

The current global need for the development of uncomplicated yet dependable gas sensors is substantial, particularly for their use in environmental monitoring, agriculture, medical diagnostics, and industrial waste management. The identification of gas molecules such as mono-nitrogen oxides (nitric oxide, NO), nitrogen dioxide (NO_2), ammonia (NH_3), carbon monoxide (CO), etc. is crucial in several domains, particularly in environmental monitoring, because of their harmful nature and the potential danger they pose to the ecosystem (Chatterjee *et al.,* 2015). NH_3, often known as ammonia, is a frequently generated gas in industrial settings and is notable for its unpleasant and corrosive nature. Even when exposed to low quantities, inhaling the substance can lead to coughing, as well as irritation of the nose and throat. Exposure to little amounts of NH3 in the air or liquid can lead to significant skin or eye discomfort. Direct exposure to concentrated NH3 solutions, such as those found in industrial cleaners, can result in corrosive harm, including skin burns and severe eye damage leading to blindness. Therefore, it is evident that timely identification of these gasses can help to prevent harm to both industrial personnel and the surrounding environment. Metal oxides possess a diverse range of electrical and chemical characteristics, which make them highly intriguing materials for both fundamental scientific investigations and practical technology uses. Oxides exhibit a diverse spectrum of electrical characteristics, ranging from insulators with broad band gaps to metallic and superconducting materials. This versatility makes them suitable for use in sensors designed to detect hazardous chemicals such as NH3. Moreover, the advancement of gas sensors based on metal oxides has the promise of enhancing worker safety and bolstering environmental protection efforts (Batra *et al.,* 2014).

Graphene and its derivatives have been extensively studied in academia for over four decades due to their susceptibility to gas sensitivity (Bose, *et al*., 2023; Guex, *et al*., 2017). Graphene has unique properties that make it ideal for use in flexible electronics, energy storage devices, and sensors. Its durability and flexibility make it ideal for use in flexible displays and wearable devices. Due to its remarkable transparency and conductivity, it is an ideal choice for touchscreens and solar cells. Gas sensors are becoming essential in various fields, such as ensuring safety in homes, monitoring greenhouse gases, controlling industrial processes, evaluating vehicle emissions for pollution control, maintaining public security, imitating human sense of smell in medical applications, and assessing chemical warfare. Furthermore, gas sensors play a vital role in identifying breaches in pipelines and storage tanks, as well as monitoring the air quality in interior settings. Gas sensor technology's progress persists in propelling innovation across diverse industries, enhancing efficiency and safety protocols (Huang *et al.,* 2015). Advancements in sensor technology have led to the development of small and portable gas sensors, improving their availability and ease of use for various everyday purposes (Batra, *et al.,* 2014; Wang *et al.,* 2013; Lai, *et al.,* 2011; Yu, *et al.,* 2010; Zhenmin, *et al.,* 2009). Nanomaterial-based gas sensors offer superior sensitivity, selectivity, and response time compared to traditional sensor technologies (Tiemann, 2007; Zhao *et al.,* 2008; Sun, *et al.,* 2015; Sun, *et al.,* 2014; Gao, *et al.,* 2013). Their small size and efficient energy consumption make them compatible for integration into wearable devices or applications associated with the Internet of Things (IoT). Advancements in gas sensor technology have the potential to revolutionize fields such as environmental monitoring, industrial safety, and healthcare (Sitakshi Gupta and Chhaya Ravikant, 2018; Cui, *et al*., 2012; Wang, *et al.*, 2016; Anasori, *et al*., 2014; Sun, *et al*., 2015; Huang, *et al.*, 2015; Korotcenkov, 2007).

Metal oxide semiconducting gas sensors are gaining interest due to their potential to impact human health and environmental safety. These sensors, made of metallic oxides with a high surface area-to-volume ratio, enable efficient gas movement through tiny openings, improving reaction speeds and performance even at extreme temperatures (Sun, *et al*., 2015; Sitakshi Gupta and Chhaya Ravikant, 2018). In recent years, graphene and its derivatives, like pristine graphene (PG), graphene oxide (GO), reduced graphene oxide (RGO), etc., have been reported to have sensing applications. Additionally, the unique electronic properties of graphene allow for sensitive detection of gas molecules at low concentrations (Lu, *et al.*, 2006). Graphene, a high-quality material with a large sensing surface area per unit volume, has the potential to create gas sensors with high sensitivity and reliability. Its unique electrical characteristics, including charge carrying and energy bandgap modification, make it an ideal candidate for sensitive and discerning gas sensors. Its elevated electron mobility and large surface-to-volume ratio further enhance its gas sensing capabilities. These attributes make graphene an ideal material for advanced gas sensor technologies, allowing for efficient gas adsorption and detection at normal temperatures (Xiao, *et al*., 2018). Reduced graphene oxide (rGO) is a superior gas sensing material due to its numerous functional groups and imperfections. The reduction of GO results in rGO, which enhances gas-sensing characteristics by increasing its surface area and adsorption capacity. This makes it ideal for detecting small amounts of gas in various settings. Additionally, rGO's unique configuration allows for enhanced selectivity and quicker reaction times compared to other gas sensor materials (Mohan, *et al*., 2018). The limited application of GOs in device physics presents a challenge for chemists who find the capability of building heterogeneous structures interesting (Bose *et al.*, 2023).

Factors influencing sensitivity

This study focuses on the use of reduced metal oxide and metal oxide gas sensors, which are widely used for gas detection due to their exceptional sensitivity and selectivity (Korotcenkov, G. 2007). Metal oxide gas sensors utilize gas adsorption and surface reactions on metal oxide surfaces, which can be influenced by factors like base materials, surface areas, microstructure, surface additives, temperature, and humidity. Scientists are working to improve the effectiveness and reliability of these sensors by investigating materials, refining sensing layer structures, and exploring innovative surface additives. They are also studying the impact of temperature and humidity on sensor responses to improve stability and accuracy in real-world situations. This progress in sensor technology has improved sensitivity and selectivity in gas detection, enabling precise detection for environmental monitoring and industrial safety (Barsan *et al.*, 2007; Korotcenkov, 2008; Batzill, 2006; Barsan, *et al.*, 1999; Park and Akbar, 2003; Batzill and Diebold, 2005; Moos, *et al.*, 2009; Rumyantseva and Gas'kov, 2008; Lee, 2009; Fergus, 2007; Lu, *et al.*, 2006; Orton and Powell, 1980; Rothschild and Komem, 2004; Comini, *et al.*, 2009; Korotcenkov, 2005; Yamazoe and Shimanoe, 2009; Tiemann, 2007; Eranna, *et al.*, 2004).

The importance of sensitivity in gas sensors has led to extensive efforts to improve it, but the inconsistent use of the term can cause confusion and difficulties in comparing different gas sensor sensitivity (Majhi *et al.*, 2021). To address this problem, efforts are being made to define a universally accepted definition and measuring technique for the sensitivity of gas sensors. By reaching a consensus on these factors, researchers can accurately assess and compare the performance of different gas sensors, ultimately resulting in improvements in their sensitivity and overall efficiency (Korotcenkov, 2005).

Metal oxide-based chemical sensors (MOSs)

Metal oxide compounds, including SnO_2, WO_3, In_2O_3, ZnO_5 and Cu_2O, are very suitable for detecting pollution gases such as carbon monoxide, nitrogen dioxide, and sulfur dioxide. These materials exhibit a notable degree of sensitivity and specificity, rendering them very suitable for applications that include the detection of gases. Moreover, metal oxide materials have rapid response times and little power consumption, making them very suitable for application in portable gas sensors. Their capacity to function at ambient temperatures further amplifies their use for diverse environmental monitoring applications (Majhi *et al*., 2021). However, pure ZnO has limited sensitivity at ambient temperatures, making it preferable to use low operating temperatures for efficient identification. Lower operating temperatures would enhance the ability of pure ZnO to detect formaldehyde gas (Guo, 2019; Gupta and Ravikant, 2018).

Reduced graphene oxide (rGO)

Reduced graphene oxide (rGO) is a promising material for gas sensing due to its thermal stability and absence of oxygen functional groups. Its weight loss is only 11% when exposed to temperatures up to 800 °C. Combining rGO with metal oxides could improve gas detection performance, as they are slow to respond and recover. However, this work has not investigated the use of rGO in combination with other materials or metal oxide composites beyond nanofibers (NFs). Mixing rGO with other metal oxides in different forms, like nanoparticles or thin films, might provide gas sensing properties not explored in this study. Several gas sensors based on rGO have been developed to effectively detect volatile organic compounds. The better ability to sense gases is due to the metal oxide/graphene-based hybrid nanostructures and oxygen-containing functional groups in rGO (Chatterjee, *et al.* (2015). Nevertheless, there are still obstacles that need to be tackled, such as improving the resilience and uniformity of these sensors and reducing production expenses. Future research should give priority to integrating these sensors into wearable devices to enable real-time monitoring of air quality and human health. Furthermore, investigating the possible use of artificial intelligence to enhance sensor precision and instantaneous data processing would be advantageous in improving this technology for practical use in many sectors (Bose *et al.,* 2023).

Synthesis of Graphene-based Nanocomposites

Graphene-based nano composites are a promising solution for improving mechanical, electrical, and thermal properties in various applications. These nanocomposites are formed by combining graphene with a matrix material, resulting in enhanced strength, electrical conductivity, and heat dissipation. Techniques like chemical vapor deposition, liquid-phase exfoliation, and electrochemical deposition are used to manipulate the dispersion and organization of graphene within the matrix material. This allows for customization of characteristics and performance in the resulting nanocomposite product. By optimizing the manufacturing process, researchers can achieve desired properties like enhanced strength or better thermal conductivity. The potential applications for these materials are vast and will continue to grow as research in this area progresses (Park and Akbar, 2003). The choice of matrix material and the distribution of graphene within it determine the properties of nanocomposites. The dimensions and configuration of graphene layers also affect their efficacy. Scientists can customize nanocomposites to meet specific application requirements by manipulating these variables. Current research focuses on developing scalable and economical methods for large-scale production of graphene-based nanocomposites, broadening their potential applications across various sectors. Graphene nanocomposites, or nanohybrids, are used for chemical detection, particularly in detecting explosive, harmful, and inflammable gases. Combining diversified metal oxides with graphene-based materials offers high sensitivity and selectivity, making them ideal for industrial safety and environmental monitoring. Their light weight and flexible nature also allows easy integration into wearable devices for personal gas detection applications (Anasori *et al*., 2014; Barsan, *et al*. (2007). This review discusses recent advancements in the synthesis and performance of reduced graphene oxide (rGO) in gas sensing, highlighting its unique properties and versatility. It also examines the performance of reduced graphene oxide and its nanohybrids.

Results and Discussion

In recent years, researchers have been paying a lot of attention to metal-oxide loaded graphene or RGO hybrid architectures for highly sensitive, selective, and cost-effective gas sensors that will operate at room temperature.

Additionally, the nanohybrid architectures show enhanced performance compared to traditional gas sensors, making them a promising avenue for further research and development in the field (Lee, 2009). Nevertheless, it is important to acknowledge that these accomplishments are currently limited to laboratory experimentation, and further extensive study is required to advance these advancements to an industrial level. The main obstacles to this are the absence of high-quality, replicable thin films, the unevenness of film thickness in bi-layer or tri-layer graphene, the high sheet resistance for layers that are tens to hundreds of nanometers thick, the lack of active groups making it relatively inert to the atmosphere, and its sensitivity to humidity. To surmount the problems, the next efforts should concentrate on the subsequent matters: There is an urgent need for a simple and inexpensive method to process single- and few-layer graphene. Furthermore, it is crucial to limit substrate effects to prevent the occurrence of unwanted surface contamination that may arise during microfabrication operations. Furthermore, it is necessary to develop novel functional molecules that possess targeted interactions with graphene in order to boost the selectivity and sensitivity of the adsorbates, hence improving the overall sensitivity of these sensors. Additionally, it is necessary to accurately measure and regulate the impact of humidity on the functionality of these sensors. (Chatterjee *et al.,* 2015).

Characterization of rGOs materials

Gas analysis uses methods like SEM, XRD, XPS, and N2 sorption to study their physical and chemical properties. These techniques help researchers understand gas behavior, pore size distribution, and chemical composition. This information is crucial for environmental monitoring, industrial operations, and material creation, as well as for developing more efficient gas storage and separation technologies. The use of these techniques enhances our understanding of gases in various settings (Kumar *et al*., 2008). Understanding the behavior and interactions of gases at a microscopic scale is crucial for developing efficient energy storage materials and gas separation procedures. This knowledge can advance renewable energy sources, improve environmental monitoring, and strengthen pollution control methods. By understanding the molecular-level behavior of gases, scientists can enhance industrial procedures, reduce greenhouse gas emissions, and develop creative solutions to tackle urgent environmental issues. Thus, a comprehensive understanding of gas interactions can lead to more efficient energy generation and storage technologies (Wang *et al*., 2013).

The study explores the gas detection capabilities of reduced graphene oxide (rGO) structures using two techniques: modified tours and modified Hummers. The modified tour method involves thermal treatment of graphene oxide, creating rGO structures with precise control over oxygen-containing functional groups. The modified Hummers technique involves oxidation of graphite to produce GO, which is further reduced to yield rGO using various reducing agents. Both methods offer unique advantages and can be customized for specific applications. The study also examined variations in electrical response of buildings with rGO under different conditions. Results showed significant differences in gas detection capabilities based on environmental conditions, suggesting rGO's potential for monitoring air quality and pollution management. Understanding the relationship between environmental factors and rGO's gas detection capabilities could lead to more efficient and reliable gas sensing devices (Gupta and Ravikant, 2018).

Applications

Metal oxides have been studied for gas sensitivity, but graphene has gained attention as a potential material due to its susceptibility to changes in electronic characteristics. Despite its excellent sensitivity at low gas concentrations, its sensor selectivity is inadequate, limiting its practical applications.

Application of graphene as strain sensors

Graphene, a single carbon atom sheet, is being explored as a strain sensor due to its high tensile strength and flexibility. Its electrical conductivity allows it to detect even the slightest strain changes, making it highly sensitive for applications in aircraft, robotics, healthcare, biomedical, artificial skin, and pharmaceutical sectors. Laser-scribed graphene strain sensors have been developed, offering flexibility in tailoring their capabilities to specific industrial demands by adjusting the thickness of the reduced graphene oxide sheet (Anasori *et al*., 2014).

Bio-sensors

Biosensors are increasingly being used in various fields, including food and the human body, to detect biological molecules. They have revolutionized diagnostics by providing quick and precise results, making them essential for industries like agriculture, healthcare, and environmental monitoring. Advanced nanomaterials, such as carbon nanotubes and graphene, enhance the sensitivity and efficiency of biosensors, allowing for greater sensitivity and selectivity in detecting specific biological components. These portable and user-friendly biosensors are being developed for diverse environments, offering advantages such as selective detection, exceptional precision, and the ability to identify analytes even at low concentrations. The integration of biosensors with artificial intelligence technology can transform healthcare and diagnostics by enabling faster, more precise diagnostics, customized treatment strategies, and improved patient outcomes. Nanomaterials also reduce biosensor dimensions, allowing for continuous surveillance and rapid identification of diseases in wearable devices. This integration can lead to predictive analytics and personalized medical treatments tailored to individual genetic composition and lifestyle choices (Adhikari and Majumdar, 2004).

Environmental Monitoring

Environmental surveillance is the process of detecting and analyzing pollutants like carbon dioxide, methane, and volatile organic compounds (VOCs) to assess air quality and identify potential pollution sources. It helps understand the impact of these pollutants on ecosystems and human health. Environmental monitoring systems provide up-to-date information, which can be used to develop effective pollution management strategies and inform policy decisions. By analyzing trends in pollutant levels over time, these systems can predict future pollution events and take proactive measures to mitigate their impact. The collected data can also be shared with the public to raise awareness about air quality and encourage individuals to reduce their own pollution contributions. (Capone, *et al.*, 2000; Gupta and Ravikant, 2018).

Industrial Safety

Industrial safety is crucial in all industries, requiring advanced monitoring systems to detect and measure dangerous gases. Regular inspections and repairs of equipment are essential for maximum performance and minimizing accidents. Workplace safety regulations and instructional programs are crucial for staff training and emergency preparedness. Advanced surveillance systems detect and measure gases like hydrogen sulfide, ammonia, and chlorine, providing immediate data on gas concentrations. Alarms and automated shutdown procedures can alert staff to potential hazards. Proactive safety plans can mitigate accidents, minimize operational disruptions, and enhance productivity and profitability (Chatterjee *et al.,* 2015).

Healthcare Applications

Gas sensing is utilized in medical diagnostics for early disease detection and monitoring vital signs, providing real-time data for remote patient care. Wearable devices in healthcare apps monitor physical activity, sleep habits, and overall well-being, offering insights for lifestyle changes and treatment strategies. Telemedicine eliminates in-person visits for patients (Barsan *et al*., 1999; Chatterjee *et al*., 2015).

Air quality management

The procedure is crucial for assessing air quality in metropolitan areas by identifying pollutants and harmful gases. It helps monitor levels of particulate matter, ozone, carbon monoxide, and nitrogen dioxide, and evaluates overall air quality. It also helps identify pollution sources and implements effective strategies to mitigate them, enhancing air quality standards. Air quality management systems are essential for reducing pollutants' impact on human health and the environment (Capone *et al*., 2000; Gupta and Ravikant, 2018).

Agricultural Monitoring

Gas sensors are essential tools for monitoring soil health, detecting pesticides, and ensuring optimal agricultural conditions. They provide real-time data on pH, moisture content, and nutrient levels, enabling farmers to address issues and prevent crop harm. They can also monitor levels of gases like carbon dioxide and methane, enabling informed decisions about nutrient management and pest control. They can also detect pesticide residues, ensuring environmental sustainability. Gas sensors also monitor soil oxygen levels, crucial for root formation and plant growth. This data helps farmers adjust irrigation and aeration procedures to maintain optimal agricultural conditions. These sensors promote sustainable farming practices and enhance crop productivity (Lee, 2009; Chatterjee *et al.,* 2015).

Industrial Processes

Integrating gas emission monitoring and control into industrial processes, like chemical manufacturing, ensures real-time emission surveillance, environmental compliance, and proactive emission reduction measures. This approach leads to financial savings, resource efficiency, and reduced waste, improving environmental impact and overall industrial operations efficiency (Chatterjee *et al*., 2015; Gupta and Ravikant, 2018).

Energy Sector

The energy industry is utilizing advanced monitoring technologies like remote sensors and drones to monitor and detect gas leaks in pipelines and storage facilities, thereby reducing environmental risks and explosion risks. This technology enables swift leak identification and correction, safeguarding the longevity of energy infrastructure (Lai *et al*., 2008).

We discuss the different synthesis methods, sensing mechanisms, and performance characteristics of these hybrid materials, highlighting their advantages and limitations. Additionally, we explore future research directions and potential applications of graphene-metal oxide nanohybrids in the field of gas sensing technology. Additionally, the nanohybrid architectures show enhanced performance compared to traditional gas sensors, making them a promising avenue for further research and development in the field.

The combination of graphene with metal oxides offers unique properties that can be tailored for specific gas detection requirements, opening up new possibilities for advanced sensor technologies.The advancement of graphene sensors is limited to laboratory experimentation and requires further study. Obstacles include lack of high-quality thin films, uneven film thickness, high sheet resistance, lack of active groups, and sensitivity to humidity. Next steps should focus on simple, inexpensive processing methods, limiting substrate effects, developing targeted functional molecules, and accurately measuring humidity impact on sensor functionality.Gas studies employ techniques like SEM, XRD, XPS, and N_2 absorption to analyze physical and chemical properties of gases. This understanding aids in environmental monitoring, industrial processes, material synthesis, and efficient gas storage and separation technologies.

Furthermore, this research can lead to the development of innovative solutions for environmental monitoring and pollution control. Understanding how rGO reacts to various conditions can pave the way for advancements in gas sensor technology that can benefit a wide range of industries.The nanocomposites were characterized using various techniques, including Brunauer-Emmett-Teller, X-ray diffraction, Fourier transform infrared, Raman spectroscopy, scanning electron microscopy, transmission electron microscopy, UV-vis spectroscopy, and X-ray photoelectron spectroscopy. The gas sensing performance was evaluated using different gases at varying concentrations, revealing promising potential due to their high surface area, well-defined structure, and efficient detection capabilities (Guo, 2019).

Gas sensing is crucial for environmental monitoring, chemical regulation, agriculture, and therapeutic applications. Metal oxides and graphene are being explored for gas sensing, but their sensor selectivity is insufficient. Researchers are exploring the use of graphene as a strain sensor due to its exceptional tensile strength and flexibility. This material is highly sensitive and suitable for various industries, including aircraft, robotics, healthcare, biomedical, artificial skin, and pharmaceuticals (Barsan *et al*., 2007; Janata and Josowicz, 2003). Overall, gas sensors play a crucial role in enhancing agricultural productivity and sustainability by providing real-time data on soil conditions. By enabling farmers to optimize their resource management practices, gas sensors contribute to more efficient and environmentally friendly farming techniques.

Conclusion

The relationship between surface reactions and gas sensing is crucial for developing more precise devices. Understanding these interactions can improve sensor performance and sensitivity. Metal oxide compounds react differently with different gases, and composite metal oxides respond better when their catalytic activities work together. Researchers are exploring nanomaterials and surface changes to enhance gas sensor sensitivity and specificity. These nanocomposite gas sensors are suitable for various chemical sensing applications.

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Conflict of interest

The authors declare that they do not have a conflict of interest.

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