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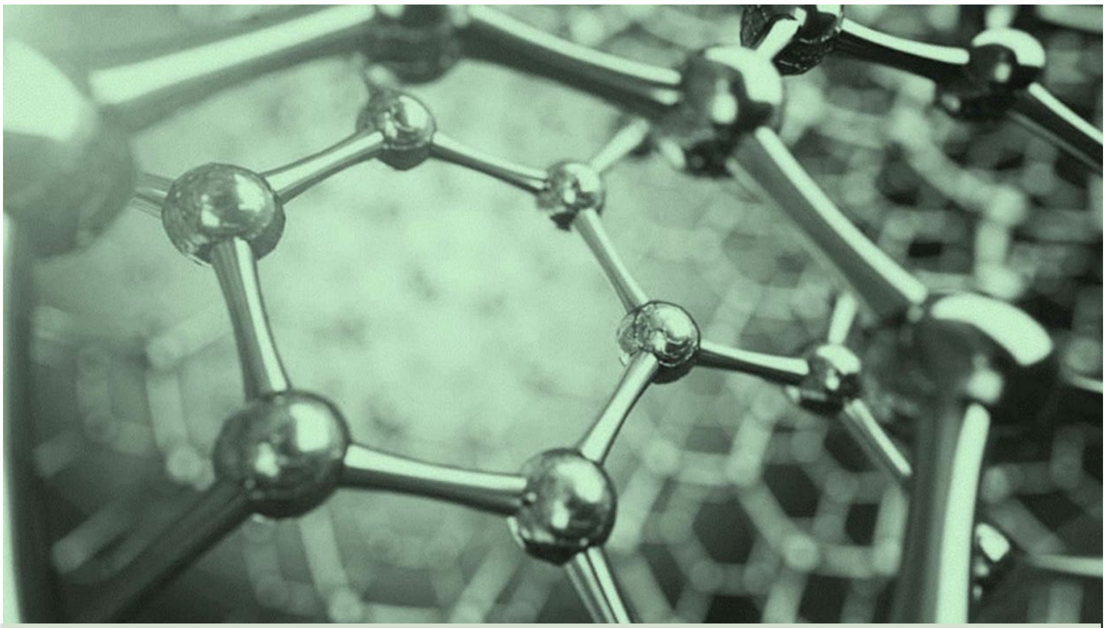

Graphene Research and Advances

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Summary

Since the discovery of graphene, it has received remarkable attention as an advanced material that has significantly influenced material science. Due to the unique atomic structure and available surface area of graphene, it has brilliant thermal, electrical and mechanical properties. These special properties of graphene and other graphene-related 2D materials allow them to be utilized in many different applications mainly in energy storage, electronics and composites applications. Consequently, a wide range of technologies such as automotive, aerospace and biomedicine have been revolutionized by implementing graphene-related 2D materials. And still, great prospects related to employing these advanced materials in different sustainable approaches are seen which can potentially bring great value to industrial development and likewise daily life.

In this edition of SIO Grafen, a few important issues from selected interesting articles concerning graphene-related 2D materials and their applications are briefly presented. The following topics are discussed.

- Graphene noncovalent functionalization can effectively modify bitumen to make it phase compatible without having any sedimented components. This increases bitumen performance which is considerably required in road construction applications.

- Doping *hierarchically porous carbon monoliths* by graphene oxide materials at a specific composition allows them to be effective composites in terms of sorption capacity and porosity properties which are favorable properties in CO_2 capturing and H_2 storage technologies.

- Utilizing reduced graphene oxides together with nanocellulose materials provides feasibility to construct high performance flexible all-solid-state supercapacitors as a new class of capacitors. One of the great advantages of this type of capacitor is its sustainability aspects due to the biodegradable and abundant cellulosic materials that are utilized in this method.

- Loading a small fraction of graphene within *organic phase change materials* provides great effectiveness of the composite in terms of thermal conductivity, energy storage, and solar-thermal-electrical energy conversion properties.

- Magnetocaloric composites based on graphene binders retain enhanced thermal conductivity and mechanical performance, which are required properties in energy conversion applications in magnetic refrigerators and thermomagnetic generator technologies.

Introduction

Industries in all sectors compete to provide the best solutions to meet the needs of societies. Their competition basically relies on research findings and innovations. In this context, SIO Grafen as one of the strategic innovation programs in Sweden has actively endeavored to cover the gap between academic research works and the needs of industries toward maturity, growth, and development. One approach to this effort is the periodic report *Research Intelligence and Advances* that is released by SIO Grafen twice a year. Hereby, SIO Grafen addresses a few interesting efforts that are performed within two-dimensional (2D) materials, specifically graphene and its derivatives such as graphene oxide (GO) and reduced graphene oxide (rGO) which are recently published in high-ranked scientific journals.

Taking advantage of advanced materials and making knowledge about their modification aiming at manipulating their full potential perfectly in various fields of applications are counted as crucial factors toward sustainable development. This explains the immense rise in the number of yearly scientific publications regarding 2D materials from 1900 in 2004 to 49100 in 2021, as reported by the Web of Science. According to the database of the Web of Science, the number of graphene-related articles has also been more than 50000 during 2011 to 2022 which indicates the rapid penetration and development of graphene-related 2D materials in different fields of applications.

Due to the inherent excellent properties of graphene and its derivatives, they can remarkably be employed in a wide range of applications including energy conversion, energy storage technologies-flexible supercapacitors, pollution treatment-CO_2 capturing, composites and coatings, biomedical technologies-regenerative medicine and tissue engineering. End-user industries including automotive and transportation, aerospace, electronics, military and defense, etc can strongly benefit from these applications. However, a lot of research on these materials is still required concerning their sustainable production methods, structural modifications to achieve even better properties and performance, finding new areas of applications based on recent modifications, and sustainability aspects including economic, social, and environmental aspects, which should be relied upon valid standards.

A graphene market analysis by Zion Market Research revealed that the global graphene market size has an expandable trend. This value for the years 2020 and 2022 accounted for USD 71.0 Million and USD 175.9 Million, respectively. This value is forecasted to reach USD 785.2 Million by the year 2028 at a compound annual growth rate (CAGR) of 35.0%. Zion Market Research reported that the key growth factors in this forecasting period are the growing demand from the electronic and automobile industry, semiconductors, and water treatment and desalination.

In this report, SIO Grafen selects the outcomes of a few interesting recent research works in which graphene-related 2D materials, as crucial materials, are employed at low values of loading to achieve fascinating results that are applicable in relevant industries. These studies are presented separately with a focus on energy conversion, CO_2 capturing, H_2 storage (energy storage), bitumen and road construction, regenerative medicine and sustainable production method of rGO.

Examples of recent research and advances

Production of rGO from discarded dry batteries

Due to the superior properties of graphene and its derivatives including GO and rGO, they take attention in different fields of applications such as medical technologies, solar cells, water distillation and energy storage. In this regard, different methods have been presented to produce these materials such as chemical vapor deposition (CVD), epitaxial growth and microchemical exfoliation. However, applying these methods to produce graphene and its derivatives are associated with some environmental impacts. One of the reasons is employing carbon feedstocks as raw materials that are needed for production. In addition, the use of chemical-reducing agents that facilitate chemical processes is not desirable since they are explosive, toxic, and harmful to the environment. Therefore, in this context, searching for other sustainable alternatives to substitute with scarce raw materials to fabricate graphene and its derivatives is essential.

A cost-effective and environmental method to produce rGO nanosheets is recently developed in a research work via anodic exfoliation of graphite in $(NH_4)_2S_2O_8$ aqueous solution. The method takes advantage of graphite rods of discarded cell batteries since these discarded batteries are not chargeable after their service-life, which means that the method includes waste management considerations in itself. In addition, the method, which offers an acceptable production rate of rGO, is an environmentally friendly method since no explosive and toxic reducing agent is used in this method. Thereby, this method can be presented as a sustainable, cost-effective, safe and simple method that has great potential for fabrication of green rGO at large scales and high production rate in applications such as electrochemical energy storage, printed electronics, solar cells and sensors.

A. Khan et al., J Mater Sci: Mater Electron 34:62, (2023)

Bitumen and road construction application

Bitumen is used in road construction to a large extent and is derived from crude oil. The main four molecular groups that constitute bitumen are saturates, aromatics, resins, and asphaltenes. The solid fraction of bitumen is asphaltene, which is also known as asphaltene nanoaggregates and includes a few number of stacked molecules that are interacting with each other. In addition, asphaltene aggregate is also formed due to interactions between those four molecular groups in the bitumen. Since asphaltene aggregates have a colloidal structure, the bitumen also has the same colloidal structure. In bitumen, resins act as surfactants and stabilize the asphaltene aggregates.

The colloidal structure and complex molecular structure of bitumen result in its weak performance in terms of thermal conductivity. Moreover, bitumen molecular structures suffer in response to temperature and moisture changes due to the huge changes within the molecular structures of bitumen. These changes adversely affect its performance in different areas of its applications. To overcome these flaws, incorporating some additives such as graphene derivatives into bitumen is suggested with respect to their excellent properties such as thermal conductivity, viscoelasticity and mechanical strength. However, the drawback with addition of graphene derivatives to bitumen is the precipitation of all the solid phases in bitumen which results in an irreversible adsorption of asphaltene aggregates onto the graphitic structure. Hence, the application of graphene derivatives to bitumen without considering modifications has inimical effects on the performance of bitumen.

In recent research, the addition of functionalized graphene to bitumen is suggested to make the bitumen structure *phase compatible*. The graphene surface is functionalized through the Molecular wedging method in which 1-pyrene butyric acid (1-PBA) is noncovalently attached to the graphene surface to provide -COOH tethers. This results in the formation of tethered asphaltene aggregates at the -COOH tethers. Finally, the novel hybrid structure which is called the PBA-graphene ensemble and includes the PBA-graphene and tethered asphaltene aggregates is constructed. The experimental results show that this new hybrid structure has phase compatibility with asphaltene aggregates, which is a great improvement in increasing bitumen performance.

Noncovalent functionalization of the graphene surface is the critical point in this approach since it allows the sp^2 hybridization of the graphene structure to be maintained while taking advantage of the effect of this hybridization in improving the graphene properties such as thermal conductivity and mechanical strength. Besides, this method introduces a cost-effective and environmental strategy to incorporate graphene derivatives within bitumen structure.

G. Induchoodan et al., Colloids and Surfaces A: Physicochemical and Engineering Aspects 660, 130865 (2023)

CO_2 capturing

Global warming is one of the hot topics that attract a lot of awareness due to its adverse consequences on the climate. In this context, there are many different materials that contribute to global warming, but the primary material that has a huge impact on global warming and is resulted as an unwanted emission, from different industries and activities is carbon dioxide (CO_2). In order to control the CO_2 emissions and decrease its impacts, a promising technology, which is known as *adsorption-based Carbon capture and storage (CCS)*, has been introduced and applied especially for capturing CO_2 after combustion which effectively decreases the emissions from power stations and industrial plants.

One of the critical points in capturing CO_2 via adsorption processes is providing a gas-solid contact configuration. So far, a few drawbacks related to the existing configurations are presented. For instance, high-pressure drops of particles, poor heat transfer in the contact area, and the limited degree of adsorption capacity of particles. Another important limitation within a gas-solid contact system is the cost-effectiveness of the regeneration process of the sorbent bed/reactor which is performed via operating temperature and pressure. Besides, some factors such as thermophysical properties of adsorbent and generated heat of reactions affect the applied regeneration method. Therefore, producing knowledge about the factors in connection with regeneration methods is crucial.

Another challenging area in this context is the selection of adsorbent material. Activated carbons (ACs) are a promising solid sorbent material for capturing CO_2 for many reasons; for example, they have exceptional thermal and chemical stability and they are also easy to regenerate. However, studies show that ACs have poor thermal conductivity (TC) which can result in adverse (heat and mass transfer) performance of the reactor in the CCS systems. As a solution to this problem and with the aim of improving CO_2 capturing, the synthesis of adsorbent composites is suggested in a few types of research via the addition of thermal conductive enhancers (TCEs) such as graphite or graphene nanoplatelets to the adsorbent bed using a proper binder. However, there is inadequate data regarding studies of the thermophysical properties and thermodynamic parameters of these composites which are accounted as central factors for designing and developing adsorbent composites for CO_2 capture applications.

In a recent study, a series of different adsorbent composites, with respect to different additives and mass fractions, were synthesized in order to study the improvement of the thermophysical and transport properties of the composite systems without losing the efficiency of CO_2 capturing at the same time. Among the various constructed combinations of adsorbent composites, a system with a coconut shell-derived activated carbon (CSAC) as the parent material, graphite as the additive, and polyvinyl alcohol (PVA) as the binder with a composition ratio of 50:40:10 wt%, respectively, showed the best result. The maximum thermal conductivity of 1.72 W/m K is obtained in this system which is a great improvement compared to the previous thermal conductivities of 0.22, 0.74, and 1.55 W/m K reported in the literature. Furthermore, the research suggests a comprehensive mathematical method to estimate the thermodynamic parameters and thermophysical data of adsorbent systems. Providing these data is central to the actual design of the adsorbent systems aiming at CO_2 capture applications.

Gautam et al., International Journal of Heat and Mass Transfer 203, 123796 (2023)

H_2 storage and CO_2 capture applications

CO_2 capture is an attractive field of research due to the problems associated with unintended consequences of CO_2 which comes mainly from fossil-based energy sources. This motivates the introduction of new fields of energy sources with less environmental impacts compared to the dominating fossil-based energies. In this context, hydrogen (H_2) is introduced as a future source of energy that is also known as a renewable and environmentally friendly energy source. However, H_2 storage is problematic due to problems such as liquefaction or compression requirements.

In the field of gas storage applications, graphene attracts attention due to its unique properties such as thermochemical or surface modification properties which allow it as an effective alternative to adsorption, separation and capture applications. However, graphene is not efficient within H_2 storage. As a solution to this deficiency, the synthesis of graphene-based porous materials with hierarchical porosity is suggested in a few research works.

Recently, several hierarchically porous carbon monoliths (HPCM) doped with GO have been synthesized and their performance investigated for the purpose of CO_2 capture and H_2 storage. Through the pyrolysis, the GO is reduced to graphene and incorporated into the HPCM matrix to make it efficient for the sorption process. High rates of H_2 and CO_2 sorption of HPCM are obtained at 10 wt% of GO addition, i.e., 9.6 mmol/g and 4.6 mmol/g respectively which are comparable with commercial materials that are used in this area. In addition, the great advantage of this modification in the synthesis of HPCM material is the replacement of graphene with binder material which is not favorable due to their adverse impacts on porosity properties and sorption capacity.

G. Zelenkova´ et al., Journal of CO2 Utilization 68, 102371 (2023)

Energy storage-flexible supercapacitors

Flexible all-solid-state supercapacitors (FASCs) attract a lot of attention in energy storage applications due to their ultra-high power density, fast charge-discharge rate, long life cycle and excellent foldability characteristics. Conventionally, oil-based materials have been widely used to produce most of these FASCs which are reasons that these production methods are considered non-sustainable production approaches. In this regard, searching for other production methods, and utilizing more sustainable materials to produce FASCs is becoming a hot topic of research considering the enhancement of FASCs performance and minimizing environmental impacts of input materials.

In a few research works, nanocellulose materials, as important base-material, in conjunction with various electrochemically active materials such as rGO are employed to construct FASCs. Comparing petroleum-based materials that have been used in this field, applying nanocellulosic materials including cellulose nanocrystals (CNCs) and cellulose nanofibers (CNFs) are advantageous due to their exceptional mechanical and hydrophilicity properties. Moreover, they are abundant and sustainable materials with respect to their promising biodegradability characteristics.

Recently, researchers applied a one-pot method to fabricate a sustainable composite membrane using CNC, CNFs and rGO materials. The research introduces a novel sustainable approach in designing the next generation of nanocellulose-based flexible energy storage devices considering the outstanding performance of the constructed membrane in terms of the volumetric specific capacitance and energy density of the FASCs which are reported to 164.3 $F.cm^{-3}$ and 3.7 $mW.h.cm^{-3}$, respectively.

Z. Ding et al., International Journal of Biological Macromolecules 228 (2023) 467–477

Energy conversion-organic phase change materials

Solar energy, which is known as one of the clean and renewable energy sources, is a valuable alternative source of energy to fossil-based energies concerning its environmentally friendly aspects. In this regard, constructing new functional materials is crucial to efficiently take advantage of solar energy in a wide range of applications such as solar-thermal energy conversion and thermal energy storage systems. An example of such functional materials is paraffin wax which is categorized in *organic phase change materials (PCMs)*.

The phase transition characteristic of PCMs allows them to reserve and release thermal energy and consequently makes them a great alternative in applications such as solar-thermal energy conversion. However, almost all PCMs have flaws in solar light absorption or thermal conductivity that confine them in applications such as solar-thermal energy conversion.

Recently, researchers developed a method to create highly thermally conductive phase change composites by designing a vertically aligned graphene/cellulose nanofiber aerogel (GCAs) and its impregnation with paraffin; this results in achieving a GCA/paraffin (GCAP) phase change composites with immense thermally conductive properties. They could achieve high thermal conductivity of 15.9 W m^{-1} K^{-1} and latent heat retention of 98% just by adding a small fraction of 3.35 wt% of graphene. Besides, a high output voltage of 823.2 mV is attained only by 5 kW m^{-2} solar light irradiation.

This work demonstrates a promising strategy for efficiently absorbing and converting solar energy, and storing and utilizing thermal energy for applications in energy-related devices and systems.

The research introduces a promising method to construct a composite employing a small fraction of graphene particles within organic phase change materials. The method shows its effectiveness to boost thermal conductivity, energy storage, and solar-thermal-electrical energy conversion properties of these types of composites which are most favorable to be applied in solar-thermal-electric energy conversion applications. The method can be presented as a solution to the associated environmental impacts resulting from fossil-based energies.

C. Shu et al., Composites Part B 248, 110367 (2023)

Energy conversion-magnetocaloric composites

During the past decades, many developments occurred in the area of energy conversion by introducing prototypes of magnetic refrigerators (MR) and thermomagnetic generators (TMGs) which are known as innovative and eco-friendly energy conversion technologies.

Obviously, this progress has only been made through discovery and development of new materials. In this regard magnetocaloric (MC) materials were introduced as functional materials to be used in MR technologies in order to employ their magnetocaloric effect (MCE). MCE can simply be defined as energy changes in a magnetic material when it is induced by changes of an applied magnetic field. The energy changes can occur in isothermal or adiabatic conditions. Generally, in refrigerant technologies, gas compression method is used to design refrigerant cycles. However, a more sustainable and energy efficient method in the field of refrigerant technologies is offered by using MC materials together with applying repeated magnetization and demagnetization processes. Furthermore, electrical or mechanical energies can be obtained from thermal energies and even waste heat energies (that are generated in many industrial processes) by using thermomagnetic generators (TMGs) which are based on magnetocaloric materials.

Despite all progress in the areas of sustainable MR and TMG technologies, there are still many challenges that should be prevailed in order to fully apply the advantages of these technologies. One challenge in the field of MR and TMG technologies is the need for materials that should, alongside their excellent MC properties, have good thermal and mechanical properties.

Mechanical stability and formability of these materials are crucial factors for making structures that can work properly and effectively under repeated thermomagnetic cycles. To overcome mechanical stability and formability problems of MC materials for applications in MR and TMG technologies, composites (with polymers or metals as matrix) are suggested as key solutions. However, there are still disadvantages with applying these matrices, since for example, using polymeric compounds results in decreasing the thermal conductivity and using metallic compounds results in absorbing a large part of the generated heat from MCE which are not desirable in this context. Therefore, finding an optimum matrix to benefit MC properties effectively in the field of energy conversion is demanded.

Recently, researchers have developed an advanced polymeric-based MC composite using a graphene-based material binder which makes it possible to achieve high mechanical stability together with high thermal conductivity. They enriched epoxy resin with a small fraction of thermally exfoliated graphite oxide (TEGO) in order to construct a percolation network to interconnect the MC particles and consequently raise the thermal conductivity. This can be explained by the presence of active defects of TEGO that makes it possible to be homogeneously dispersed in the matrix and binds with metallic particles. Moreover, these composites can be shaped in different desired structures, and have a high mechanical performance via the presence of graphene binders in the composition. This research presents a simple and eco-friendly method to construct MC composites with improved thermal conductivity and mechanical performance required for energy conversion applications based on graphene binders.

C. Coppi et al., Advanced engineering materials 25, 2200811 (2023)

Biomaterials in regenerative medicine

The development of nanotechnology influences the development of many other fields of science such as regenerative medicine and tissue engineering. This is mainly due to advances in the field of biomaterials that mimic biological structures using new nanomaterials, as well as exploit surface modifications of the materials that are used for these purposes. Although many nanomaterials are applied in these fields, there are still challenges in using these materials efficiently that should be conquered.

Carbon nanostructures are one of the promising candidate materials in the field of tissue self-regeneration due to their unique properties and great biocompatibility with body tissues. Among carbon nanostructures, many types of research are dedicated to the potential application of graphene and its derivatives such as GO and rGO in medical applications including drug and gene delivery systems, biomedical sensor devices, cell and tumor imaging (biosensing) particularly in cancer therapies, tissue implants and wound dressing. A series of polymeric nanocomposites which include these types of nanofillers also show bioactivity characteristics in terms of rapid growth of stem cells, including bone, nerve, heart and skin tissue, on their surfaces. In this regard, GO shows huge compatibility with a lot of polymeric systems.

In a recent research work, a method is presented to study the bioactivity of a biomembrane material. The research reported the incorporation of GO and rGO nanofillers with a poly(ε-caprolactone) (PCL) matrix to construct GO/PCL and rGO/PCL nanocomposite membranes, respectively. In this regard, Osteoblast-like cells (human U-2 OS cell line), which are most commonly used for biomedical studies, are cultivated on the surfaces of these materials. The bioactivity of the nanocomposite membranes and the cellular response on surfaces of these membranes are tested using different analytical techniques in which the two-dimensional correlation (2D-COS) Raman spectroscopy technique represents an optimal technique to characterize the interactions of nanocomposite membrane systems including its interactions with osteoblast-like cells at early stages. The results show that biocompatibility of the material is enhanced by modification of the PCL matrix using GO additives, which in turn results in the biological applications of the material which can be utilized in bone tissue engineering applications, for instance.

A. Kołodziej et al., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 285, 121862 (2023)