SIO GRAFEN

Graphene Research and Advances

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Introduction

The family of two-dimensional materials exhibits a high stability and flexibility enabling their implementations in a huge number of environments. Creating hybrids and composites would allow to equip already established materials with enhanced or even completely novel properties. For example, the most famous member of the 2D materials, graphene, is highly conducting, which makes it interesting as electron transporter for chemical processes or as conductor in flexible applications. Furthermore, the strong intralayer bonds makes 2D materials an excellent alternative to reinforce composites.

These wide spread properties are highly interesting for researchers and industrial developers and led to countless publications on graphene promising novel applications. However, due to the nature of nanocomposites and nanomaterials, the actual implementation into technologies is almost invisible. Nevertheless, over the last years several companies invested heavily in the development of graphene products. Next to industry giants, such as Samsung and Apple, many small companies rely strongly on the implementation of graphene, in particular start-ups resulting from commercial interesting research results in universities and laboratories.

These scientific studies are on the forefront of the ongoing development in graphene and 2D material technologies. Main focus lies on the improvement of existing ideas and processes, but with unconventional approaches. This can range from overcoming obstacles to apply conductive graphene ink on any substrate, to developing novel heterostructures to enhance nanocomposites. The intended field of applications is even wider ranged, including electronic products, mobile devices, design, medical, automotive and aerospace industries. This makes graphene, other 2D materials and their heterostructures an important research field, to understand how their properties are affected when implemented in or on another material, and how they can contribute in new application areas.

Content

Fabrication of large area graphene

The hexagonal graphene structure occurs naturally and can be isolated from bulk graphite using a simple cleavage technique with household scotch tape. Even though the extracted graphene flakes are usually of excellent quality, this technique is not suitable for industrial applications. So far, most industrial processes using graphene, for example in conductive inks, reinforced compounds or membranes, employ liquid exfoliation to produce large amounts of graphene flakes. Such a technique uses a liquid solvent which intercalates the graphene layers supported by ultrasonication breaking the van der Waals bonds and creating in liquid suspended graphene sheets. This liquid can be printed, mixed into compounds or dried to produce multi-interconnected graphene layers. The final products possess properties close to their mechanically exfoliated counterparts studied in the laboratories.

However, even though pure graphene and liquid exfoliated graphene are well comparable in mechanical and chemical strength, the latter has significantly deteriorated electrical properties due to the large amount of grain boundaries and multiple interlayer resistances. A promising technique to produce large scale graphene sheets with high electrical quality growth graphene on a metal catalyst by chemical vapor deposition (CVD). In a high temperatures furnace with a partial pressure controlled gas mixture graphene growth uniformly on a copper or nickel foil. The growth of graphene on copper by CVD is limited to one layer and the grain size can be well controlled reaching several millimeters resulting in high quality large area graphene. Such monolayer graphene has been shown to exhibit excellent electrical properties comparable to average exfoliated graphene and superior to any other known material. The metal foil acts not only as a catalyst but also as a carrier substrate. After the deposition the layers can be transferred to any substrate, which is a huge advantage towards substrate-dependent growth techniques. The transfer usually requires the etching of the copper foil. Even though the growth, etching and transfer has been already demonstrated from lab scale up to a 30 inch roll-to-roll technique for industrial fabrication, a large global production would require significant amounts of copper and the recycling of the etchant, which is highly unsustainable.

Kim et al. *Nature* **457**, 706 (2009)
Bae et al. *Nature Nano* **5**, 574 (2010)
Yan et al. *Acc. Chem. Res.* **47**,1327 (2014)

Over the last years, researchers from the Chalmers University of Technology studied and improved a new technique, which promises the immediate reusability of the copper foil. The scientists employed the electrochemical properties of copper by submerging the final polymer (PMMA)/graphene/copper stack in a NaOH+H_2O solution with an electrode attached to the copper sheet. Applying a voltage between the copper and a second platinum electrode in the electrolyte yields an electrolytic reaction forming O_2 on the platinum electrode and H_2 on the copper. On the graphene side, protons from the electrolyte can permeate through the graphene, where they acquire an electron forming hydrogen. Since hydrogen cannot permeate through graphene, the formed hydrogen bubbles delaminate the graphene from the copper foil. The fully delaminated graphene attached to the protective polymer can be transfer within minutes. The Swedish researchers were able to control the speed of the delamination by adjusting the applied voltage and compared the graphene quality noticing no significant changes in the properties between fast and slow delaminated graphene. However, the formation of hydrogen bubbles created a strong enough pressure to break the graphene and polymer layer. This required a subsequent optimization of the polymer layer, which could be achieved by increasing the thickness of the PMMA from 290 nm to 600 nm preventing the formation of defects on a large scale. Finally, the copper foil is completely untouched after the process and can be directly reused to grow graphene saving time and resources.

de la Rosa et al., *Appl. Phys. Lett.* **102**, 022101 (2013)
Zhan et al., *J. Mater. Chem. C* **3**, 8634 (2015)

Earlier this year, researchers from the National University of Singapore presented an alternative approach using a sustainable bubble-free transfer with a reduced defect rate. This process uses two electrodes in a NaCl solution applying a voltage lower than required for the formation of bubbles. Instead, it is based on the electrochemical reduction of adventitious copper oxide at the graphene/copper interface. This avoids wrinkles, bubbles and cracks created with the bubble transfer technique and does not exhibit contaminations as introduced by chemical etching. The researchers also confirmed the recyclability of the metal substrate for CVD growth of graphene interesting for lower prices large area film productions.

Cherian et al., *Small* **11**, 189 (2015)

Printed graphene antennas

In the last decade producers, wholesalers and customers demanded more intelligent packaging to keep their inventory simple to access, manage and safe at the same time. This led to the introduction of radio frequency identification markers (RFID tags), which consist of a simple electric circuit and an antenna. Even though these circuits are flexible and affordable, they are not cheap enough to be applied ubiquitously to replace for example bar codes. Early results on liquid exfoliated and printable graphene ink led to the first commercial applications of graphene being used for RFID tags (for example by the US based company Vorbeck). However, the printed antennas always require a carrier substrate on which they are printed and dried. Most inks to date either disperse graphene in a solvent or integrate a binder. Dispersed graphene inks do not involve a binder, but the deposited lines consist of loosely connected graphene oxide flakes, which results in a conductivity comparable to polymer-based inks making it less attractive for commercial applications. Therefore, most conductive inks rely heavily on the implementation of binders, since granular powders cannot form a continuous film without linking the grains. Nevertheless, binders are insulators and reduce the overall conductivity of the ink, which makes an annealing process at 250°C necessary to remove the binder resulting in an improved conductivity. This annealing step makes the process incompatible with heat sensitive materials, such as paper, fabric or plastic.

In May this year a research group from the University of Manchester presented a technique to produce highly conducting printed graphene antennas without a binder. The researchers used an ink made of graphene nanoflakes dispersed in a solution. After printing, they dried the ink at 70°C removing the dispersant and leaving a highly porous coating. Finally, rolling compression of the coating forms a laminate with improved linkage between the flakes in the ink resulting in a higher conductivity. The achieved conductivity is almost twice as high as previously reported in graphene inks with binder, and about ten times higher than uncompressed binder-free inks. The researchers also tested different amounts of pressure used for the rolling compression showing a linear dependence of the compression ratio to the sheet conductance. To show the practicality of this technique, the scientists printed a graphene laminated dipole antenna on a paper substrate. The measurements demonstrated the effective radiation of the antenna regarding all aspects of impedance matching, gain and radiation pattern, which shows the feasibility of compression rolled graphene laminate for printed RF applications. This result is very promising and could allow to apply flexible conductors and antennas directly on a large variety of substrates reducing the material cost and weight. Furthermore, it can also be implemented in the growing field of the “internet of things”, which will require electronic manufacturers to provide more complex logic and communication circuits for all kind of object in our everyday life.

Huang et al., *Applied Physics Letters* **106**, 203105 (2015)

From conducting textiles to strong nanocomposites

Two-dimensional materials and in particular nanocarbons, such as carbon nanotubes and graphene, possess a unique combination of electrical and mechanical properties generating significant interest for their use in composite materials. On one hand, theoretical predictions demonstrate the potential for significant improvements in strength and stiffness due to their strong intralayer bonds. On the other hand, the flexibility and electric properties of 2D material layers make them interesting for wearable or flexible electronic devices. Even though many promising results have been reported so far, the lack of reproducibility and scalability have yet to be adequately addressed.

Recently, a research collaboration between the Universities of Lisbon in Portugal and Exeter in the UK reported the transfer of monolayer graphene onto fibers commonly used by the textile industry. The graphene was grown by chemical vapor deposition on copper foil and subsequently transferred onto the fibers using the conventional large scale technique. The graphene-coated fibers have a sheet resistance as low as 1 kΩ/□, comparable to the one measured in graphene on silicon transferred by the same technique. Furthermore, the graphene-textile demonstrates a high stability under mechanical stress and bending. The researchers were able to demonstrate these properties reproducible in four samples making this the first example of a textile electrode, flexible and truly embedded in a yarn.

Neves et al. *Scientific Reports* **5**, 09866 (2015)

In contrast, a lot of effort has been invested during the recent years to use 2D materials to reinforce synthetic resins. Such resins are manufactured in a liquid state only to harden in the final shape, similar to their natural counterpart. Their applications ranges from thermosetting plastic, over epoxies to copolymers and acrylics. Mixing these materials, for example with graphene, allows to maintain their optical properties whilst enhancing their physical properties.

Recently, an Indian research group from the Anna University studied the differences in properties of the resin polybenzoxazine (PBZ) when adding various weight percentages of functionalized graphene oxide (FGO). The resulting nanocomposites were characterized for their thermal, mechanical, dielectric, and optical properties using different analytical techniques. The researchers found that an added 5 wt% FGO-reinforced PBZ composite shows a 20% higher glass transition temperature, which generally means an increased stiffness of the material and consequently an improved thermal stability (about 40%). More significantly, the electric properties of the graphene oxide strongly affected the resin almost tripling the dielectric constant compared to untreated PBZ. Furthermore, 5 wt% FGO-reinforced PBZ composite shows an enhanced ultraviolet shielding efficiency (88%) and a 50% improved tensile strength. These improvements stem from a homogeneous and uniform distribution of FGO in the PBZ matrix, as seen in scanning electron microscopic and high-resolution transmission electron microscopic images. These results are extremely promising, since nanocomposites with high dielectric constant can be used as insulating coatings, sealants, and encapsulates for high performance dielectric as well as antistatic applications.

Revathi et al. *High Performance Polymers* **0954008315585013** (2015)

Similar results have been presented just in August at the 20th International Conference on Composite Materials by researchers from Cardiff University and Haydale. The British company Haydale developed a plasma process to produce large batches of nanocarbons (hundreds of grams). Using an epoxy resin infusion process, the scientists were able to demonstrate the component scale manufacturing of large panels with adjustable properties. The nanocarbon has an effect on the epoxy resin viscosity and can be optimized to have up to 50% higher compression after impact properties. Such advances in composite material strength and stiffness are highly interesting for aerospace and automotive industries.

An alternative approach to optimize resins has been shown by a Chinese research group using carbon nanotubes (CNTs) wrapped with MoS_2 nanolayers (M−CNTs). This hybrid was incorporated into EP, one of the most important thermoset polymers. M−CNT hybrids showed a good dispersion in the EP matrix compared to pristine CNTs. The obtained nanocomposites exhibited significant improvements in thermal properties, flame retardancy and mechanical properties, compared with those of neat EP and composites with only CNT or MoS2. The char residues and glass transition temperature of the EP composite was significantly increased when incorporating 2.0 wt % of M−CNT hybrids. Furthermore, the M-CNT hybrids add excellent fire resistance to the EP matrix resulting in a significantly reduced peak heat release rate and total heat release. Moreover, the amount of organic volatiles produced in a fire was significantly decreased, and the formation of toxic CO was effectively suppressed, which implies a reduced toxicity and supressed smoke production. The dramatically reduced fire hazards were generally ascribed to the synergistic effect of MoS_2 and CNTs, the excellent dispersion of the M−CNT hybrids and physical barrier effects of MoS_2 nanolayers and CNT network structure. Such composites are interesting for a wide range of applications, from mobile devices, over interior design to automotive and aerospace industries.

Zhou et al. *Applied Materials & Interfaces* **7**, 6070 (2015)

Medical sensors

In the recent years a large trend emerged to develop individualized health care monitoring not only for medical applications, but also for personalized fitness tracking. These devices use a wide range of sensors detecting temperature, heart rate, oxygen levels, breathing, blood volume, blood pressure and skin conductivity using optical and electrical techniques. Graphene and other two-dimensional materials are ideal candidates for environmental sensors, since they offer a large surface to volume ratio combined with unique arrangement of optical, electrical, mechanical and thermal properties. However, researchers try to use the biocompatibility and flexibility of 2D materials to employ them directly on the skin to non-invasively measure several parameters of a living organism. One possible aim is the development of biologically stable films based on 2D materials with a high gauge factor, a measure describing the strain sensitivity of the material extracted from the resistance change relative to the resistance without strain.

Earlier this year, Korean scientists presented exactly such a graphene hybrid material, which demonstrates a significant improved gauge factor and pressure sensitivity calling this material “E-skin”. The E-skin is based on graphene grown by chemical vapor deposition on copper foil. After etching out the Cu and replacing it with a polydimethylsiloxane (PDMS) substrate, the scientists grew nanofibers vertically on top of the graphene using a vapor deposition polymerization process. Previously, such polymer based nanodevices have shown superior strain and pressure sensing capability than comparable bulk materials. In this case, the combination of graphene and the nanofibers exhibits additional synergetic effects compared to the individual components. Similar to hairs on our skin, the graphene/nanofiber combination enhances the contact surface area, piezo-resistive effects, gauge factor and mechanical properties, which results in ultra-sensitive strain sensing and high durability. The compound demonstrates a pressure detection limit of 0.5 Pa, which is about ten times more sensitive than previously reported, and a gauge factor about three times higher than the best result published so far. Furthermore, it is extremely durable and exhibits a reproducible performance, remaining constant over 1000 strain cycles. This means, E-skin can respond to extremely small deformation and hence detect very slight motions, such as changes in the facial expression or a pulse. E-skin is biocompatible and can be worn directly on skin. This makes such devices extremely promising for widespread individual-centered health monitoring making stationary monitoring, using optical electronics and rigid multi-electrode pressure sensors, unnecessary.

Park et al., Carbon 87, 275 (2015)

Graphene in supercapacitors

The increasing number of mobile devices, such as wearables, mobile phones and computers, demand large capacity energy storages which are quickly rechargeable at low weight and cost. So far, lithium ion batteries are widely used as secondary cells for high capacity energy storage at low weight. Nevertheless, the unstable electrolyte, low cyclability and theoretical low limited energy density (800Wh/kg) fuelled the research of novel energy storage technologies. Alternatives, such as supercapacitors and lithium-air (LiO_2) cells, have been studied for several years and demonstrate extremely fast recharge cycles and up to 20 times higher energy densities almost reaching the limit of fossil fuels (13000Wh/kg).

Supercapacitors possess a higher capacity than conventional electrolytic capacitors. They charge significantly faster, and demonstrate a high flexibility and compact design in comparison to typically rigid batteries. These properties make supercapacitors attractive for applications in flexible and ultrathin electronic devices, such as wearables and smartphones. To achieve a large capacitance, supercapacitors need a large electrode surface area and pseudo-capacitance. An applied voltage between the electrodes of an electrochemical capacitor moves the polarized ions to the opposite polarized electrode forming a double layer separated by a single layer of the solvent (generally water). A pseudo capacitance can originate when specially dissolved cations in the electrolyte pervade the double layer. Such cations store electro-chemical energy by means of a reversible redox reaction on the surface of suitable electrodes. So far, polyaniline (PANI) has been used as efficient electrode material with a large pseudo-capacitance. However, the weak mechanical properties of PANI make it unsuitable for flexible devices with repeated charge cycling. Researchers from BASF in Germany demonstrated already in 2014 that nano graphene platelets (NGP) dispersed in a solution with PANI provides a simple, cheap and inkjet printable alternative. The NGP/PANI supercapacitors exhibit excellent mechanical and electrical properties with a large specific surface resulting in a large capacity, which remained unchanged for more than 1000 charging cycles.

Xu et al. Journal of Power Sources 248, 483 (2014)

Recently, chemists from the University of Manchester used a similar technique to prepare electrodes without PANI on a polyvinylidene fluoride (PVDF) substrate using graphene and molybdenum disulphide (MoS_2). MoS_2 in particular possesses a high catalytic activity making it an efficient hydrogen evolution catalyst as well as a useful energy storage material for use in lithium ion batteries. The researchers used a liquid exfoliation technique to prepare a solution of single layer nano platelets of graphene and MoS_2, which they could apply and dry on the PVDF substrate. This resulted in flexible electrodes, which they integrated in conventional coin cells using an aqueous electrolyte (Na_2SO_4). With a constant mass loading of the electrodes the researchers were able to compare the results for individual graphene and MoS_2 based electrodes as well as their heterostructure. Surprisingly, using the graphene/ MoS_2 heterostructure as electrode material doubled the current density and increased the output power significantly. The main shortcoming of MoS_2 is the high intrinsic resistance. The graphene/ MoS_2 heterostructure combines the high conductivity of graphene with the high catalytic activity of MoS_2. The layered heterostructure also enhances the cycling stability, which is another important metric. Usually, such cells tend to lose 10-30% of capacity within the first 1000 charge cycles. Surprisingly, the researchers noticed an increase in capacity during the first 3000 cycles of up to 250%, which afterward remained unaffected for more than 7000 cycles. They explained this effect by electrochemical re-exfoliation of the electrode material yielding increased ion intercalation and consequently an increased pseudo capacity. The absence of a decreasing capacity during the 7000 cycles after the preconditioning demonstrates the practical applicability.

Bissett et al. Applied Materials & Interfaces 7, 17388 (2015)

An alternative approach was demonstrated earlier this year when Chinese scientists demonstrated an ultrahigh capacitance by developing a redox-electrolyte for conventional graphene electrodes. Usually, the specific capacity in supercapacitors using a Na_2SO_4 electrolyte originates from the electric double-layer capacity. During the oxidation reaction oxygen groups can form on the surface of the graphene sheets. These oxygen functional groups cannot be reduced preventing an additional pseudo capacitance. Adding $K_3Fe(CN)_6$ to the electrolyte forms ions, which can be reduced and generate a pseudo capacitance from the redox reaction.

Chen et al., Nanoscale 7, 432 (2015)

On top of the improved performance, both research groups from Manchester and China used no binder to produce the adhesive two-dimensional material layer, which simplifies the production and decreases fabrication costs making it even more attractive for commercial applications.