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GRAPHENE AND THE APPLICATIONS IN BULLETPROOFING AND BODY ARMOR

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Abstract *— Militaries may have found the next technology advancement, a replacement in body armor. Graphene is a single atomic layer of graphite, which is composed of a hexagonal lattice of carbon atoms. It exhibits properties of extreme strength and is extremely lightweight. Engineers have begun testing this material's successfulness in bulletproof vests. We will delve into the strengths and weaknesses of graphene in the construction of bulletproof vests for stopping projectiles, as well as the testing that has been done on the material.*

As weaponry continues to develop, it is vital to develop advanced methods of protection. The durability and flexibility of graphene prove that it can be very helpful to troops who travel through extreme conditions. With a strong, lightweight material, military units can put more effort into completing the tasks at hand, which will lead to less casualties.

We will consult a variety of resources where we can gain a better understanding of the material and its properties. We will debate the practicality of mass production of graphene and graphene products. In the paper, we will also look at ways to create a sustainable supply of graphene. We will discuss how graphene can be useful as bullet protection and how it can give an edge to our military. Lastly, we will discuss how the military can make use of the strength of graphene in vehicles and even weaponry, as well as what the development of graphene can mean for the safety of our world.

Keywords—Body Armor, Bulletproofing, Carbon Nanotubes, Graphene, Graphene Oxide, Military, Warfare

HISTORY OF BULLETPROOFING

Militaries across the globe need to provide protection for their soldiers. The first forms of armor can be traced back to the Middle Ages when knights went to battle wearing armor consisting of rigid plates that were capable of stopping blows from weaker forms of attack, such as swords and arrows. These archaic forms of armor soon became obsolete around the 1500s with the invention of more powerful ranged weapons, such as firearms [1]. The previous rigid armor was no longer effective against the concentrated shock of being shot by the higher velocity, black powder propelled rounds that emerged from the barrels of rifles. As time progressed, shock absorbing vests became more refined, with the first notable usage appearing in the English Civil War by Oliver Cromwell and his cavalry between 1642 and 1651. These double layered, metal cuirasses, or vests, were rather heavy, but proved to be very effective in battle [1].

Another notable use of this new technology was its adoption by Australian Outlaw Ned Kelly in 1880 [1]. The criminal equipped his gang with homemade armor that was constructed from steel ploughshares [1]. Weighing around one hundred pounds, it consisted of a helmet, a vest, and an apron [1]. It was worn under long coats, standing up to barrages of fire from law enforcement, denting the armor without penetrating it [1]. This new adaptation was incredibly effective, until police realized that it offered no protection to the arms and legs, resulting in the eventual demise of the Ned Kelly Gang [1]. The experimentation continued in World War I, when the United States began equipping its men with a combination of a breastplate and a helmet, also known as a Brewster Body Shield [1]. It was primarily constructed of chrome nickel steel, providing sufficient protection from incoming rifle rounds and weighing only around forty pounds [1]. While strong and semi-lightweight, the rigidity of the Brewster Body Shield seriously restricted a soldier's ability to move, making it mildly impractical. This led to a search for a more flexible alternative.

Up until the 1960s the most effective new models for bulletproofing included heavy flak jackets and other large contraptions [1]. That was until DuPont, a company based in the United States, invented flexible, strong, artificial fibers called aramids [1]. After the company's invention of its first fiber, Nomex, the bulletproofing industry was once again booming [1]. Finally, in the early 1970s, Dupont invented a revolutionary new fiber called Kevlar [1]. Vests manufactured with Kevlar are strong, lightweight, and can be easily concealed under everyday attire, making them ideal for law enforcement. The only downside to this armor included the fact that it can be penetrated by large caliber rounds, offering limited protection [1]. Unfortunately, however, after the adoption of Kevlar, the progress in searching for more effective materials has ground to a halt.

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WHAT IS GRAPHENE

Though Kevlar is currently the most useful method of body armor, a new material, graphene, which was first isolated in 2004, holds potential as a powerful substitute [2]. As the first ever discovered one-dimensional material, graphene consists of a single layer of closely packed carbon atomic rings forming a hexagonal lattice [2]. It is both the lightest material known to man and the strongest material ever discovered, making graphene very promising for the future in many areas of society [2]. Graphene comes from the splitting of the naturally occurring graphite, into thin slices until it becomes one atomic layer thick [2]. This single atomic layer holds carbon atoms together through single bonded sp2 level bonds which are 0.142 nanometers apart [3]. Graphene has many interesting properties such as a high surface area per mass of 2630 m^2/g, the strongest known electrical conductivity, an impermeability to gas, and an immense capability of transmitting light with a transparency of about 98% [3]. These properties make graphene the most highly anticipated and most useful material to be developed today.

While some scientists and engineers venture to find methods of large scale production, others have begun testing its practicality and applications into everyday life. Graphene can be advantageous in a variety of uses including electric conductivity, structural foundation, and bulletproofing [4].

CONTROLLED STUDIES

Multilayer Graphene Sheets

One of the most advantageous uses for graphene is its replacement of Kevlar in bulletproof vests. As stated earlier, the outdated aramid fibers used for bulletproofing have many flaws in design and performance. First and foremost, the vests help little in dispersing and dissipating the force applied to the wearer once the bullet has been stopped. This is a huge issue due to the fact that large rounds will exert massive amounts of force on the body, even without penetration, that can easily rupture internal organs. There is also a very large chance that high velocity or large caliber rounds will penetrate the vest completely, as most are designed to stop pistol rounds, which possess much less kinetic energy and are therefore more easily absorbed by the vests [5]. While Kevlar is a revolutionary technology providing a huge step up from its predecessors, it still does not fully protect the user, as severe blunt trauma wounds are common [5]. Stopping the bullet itself is vital, but the force that it applies must also be stopped in order to ensure full protection. Engineers and scientists have tirelessly pursued a solution for these shortcomings of Kevlar and other fibers with no substantial findings. Finally, after extensive research and testing, Researchers at Rice University in Texas believe that they may have solved this dilemma in the form of graphene [5].

Up to this point in time, testing of the super-material has been primarily related to its electrical conductivity or tensile strength. Edwin Thomas led a team of researchers at the George R. Brown School of Engineering at Rice University in Houston, that designed an experiment in which microscopic projectiles were fired at multilayer graphene sheets, giving them an accurate representation of the response of the material to similar projectiles on a macroscopic scale [5]. The sheets ranged from 10 to 100 nanometers, or 30 to 300 atomic layers, thick [6]. The nanospheres were eventually fired at speeds of up to three kilometers per hour, which is much faster than a bullet from an AK-47 [6]. Showing very promising results, the tested graphene samples proved to be strong, rigid, and elastic all at the same time [5]. The sheets exhibited unique properties, stretching into a cone and absorbing a majority of the projectile's energy before breaking [5]. This unique property is caused by the hexagonal lattice structure of graphene, consisting of tightly bound carbon atoms with very strong bonds [5].

"The game in protection is getting the stress to distribute over a large area. It's a race. If the cone can move out at an appreciable velocity compared with the velocity of the projectile, the stress isn't localized beneath the projectile," stated Mr. Thomas [5]. To summarize, the tensile stress must be distributed across a large area before it reaches the wearer. In the end, the results of the testing at Rice University was very successful, showing that tensile stress could travel through graphene sheets at a speed of 22.2 kilometers per second, and that all the energy from the bullet was completely distributed over a large area 3 nanoseconds before the sheet was punctured [6]. It was also concluded that graphene is 10 times better than steel at dissipating kinetic energy, which is a very important property regarding this specific application, a property which will be further discussed in the section addressing the applications to bulletproofing [6].

Another study at the University of Massachusetts, led by Jae-Hwang Lee, involved similar procedures and yielded equally promising results [5]. While the researchers at Rice University aimed to push the graphene sheets to their limits with extremely high-velocity projectiles, Lee's team wanted to test the material at a more realistic speed in order to calculate just how much energy it can disperse [7]. The micro-bullets were quickly and precisely accelerated, to 3 kilometers per second, by the gases produced when laser pulses were used to evaporate a gold film [7]. The researchers then measured the initial and final kinetic energy of the bullet in order to determine the amount of energy absorbed and dispersed by the graphene sheets [7]. They found this amount of dissipated energy reach up to 0.92 megajoules of energy per kilogram of graphene, which is very impressive when compared to the 0.08 megajoules per kilogram that steel exhibits [7]. These statistics, combined with the incredible lightweight property of graphene, promise it future appearances in the bulletproofing industry.

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Graphene and Carbon Nanotube Composite

While graphene sheets have proved themselves to be more than capable of stopping a speeding bullet, there is yet another form of the wonder material that may be even more effective. Researchers at the University of Wollongong in Australia have recently discovered a composite material of graphene and carbon nanotubes that has proved to be stronger than both spider silk and Kevlar [5]. Carbon nanotubes are unique formations of carbon atoms that exhibit high strength, lightweight properties, and excellent energy absorption capacity [8]. Essentially, they are rolled up tubes of graphene which can be produced much more quickly and effectively than graphene sheets [8]. When synthesizing the graphene-nanotube composite, the ratio of nanotubes to graphene is essential to making the best possible bulletproof composite, as different composite ratios possess different properties [5]. This nanotube combination is also much easier and more cost effective to produce than the previously mentioned sheets, as it can be manufactured in bulk using a wet spinning technique [5]. The most important aspect of this new composite to bulletproofing, however, is the unique structure that combines the hexagonal lattice of traditional graphene with the cylindrical structure of carbon nanotubes [5]. These cylinders are capped on each end and held together by covalent bonds, which are individually stronger than the bonds in diamond, the hardest known substance [5].

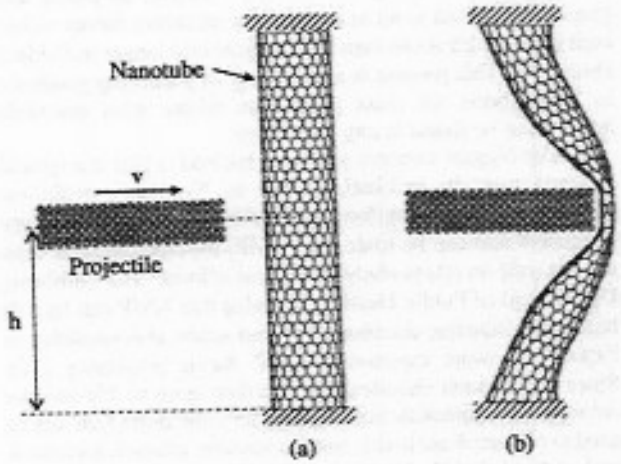


FIGURE 1 [8]
Structure and Ballistic Resistance of Graphene and Carbon Nanotube Composite

Shortly after discovering the graphene-nanotube composite, the Australian research team began testing its ballistic resistance through a controlled study [8]. Shown in Figure 1, the nanotubes were fixed at both ends to simulate being part of a composite vest, and diamond projectiles, with tip widths much larger than that of a flattened nanotube, were fired at between 1,000 and 3,500 meters per second [8]. The maximum velocity was calculated in a separate study in which the nanotubes were shot with increasing velocity until they experienced bond breakage or detachment [8]. In addition, due to the fact that projectiles would impact many different points on the nanotubes during combat, the diamond bullets were fired at points all along the face to test for weak areas [8]. Lastly, the loss of energy to heat had to be accounted for throughout the calculating, so the temperature change for the last two rows of atoms on both fixed ends was calculated [8].

The Australian team's testing yielded many interesting and insightful results. First, a bullet that strikes a fixed nanotube will ultimately result in deformation of the tube in order to absorb and disperse the energy [8]. Eventually, the tube will be broken completely after being struck multiple times, due to repeated impact regardless of the velocities of the projectiles [8]. It was concluded that a singular nanotube can only absorb a certain, fixed amount of energy before breaking, the maximum absorption being completely independent of the number of shots through which it is transferred [8]. For example, if a composite nanotube can absorb a maximum of 10 Joules of energy before breaking, it will break after being struck by eleven projectiles, each with kinetic energy equal to 1 Joule, but not after being struck by one projectile with kinetic energy equal to 9 Joules. This maximum value was found by calculating the energy difference between the nanotube before being struck by any projectiles and just before being fractured by the final projectile [8]. The graph shown in Figure 2 illustrates the relationship between the length of nanotubes and their energy absorption threshold.

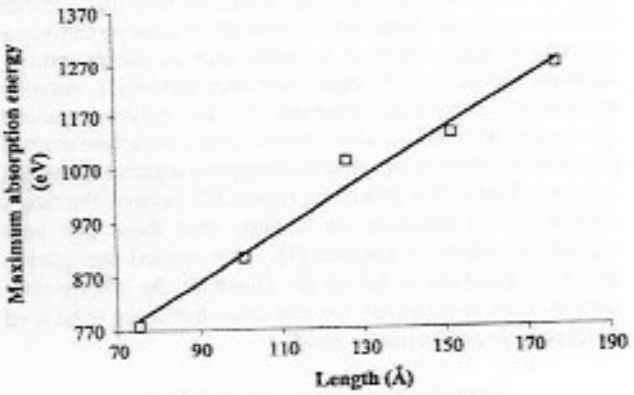


FIGURE 2 [8]
Variation in Energy Absorbed Before Breaking as Length is Changed

After many calculations and extensive data analysis, it was determined that the maximum projectile velocity that a composite nanotube could withstand, which is directly related to the kinetic energy of the bullet, was a function of the radius of the tube and the impinging location of the bullet [8]. For clarity, the impinging point is defined as the distance between the point of impact and the end of the tube divided by the

length of the tube [8]. To summarize, a longer tube, a larger radius, and a shorter distance between bullet impact location and the center of the tube cause a greater resistance to the rupture of nanotube by the projectile. Another notable finding is that the previously discussed correlations are not valid if the projectiles strike one after another, with almost no time in between impacts [8]. If the diamond bullet struck within 12.5 picoseconds of the last strike, the tube would respond unpredictably, breaking the majority of the time [8]. This is due to the composite material's limited capacity to disperse the energy in such a short time [8]. Regardless, the team at the University of Wollongong concluded with very high certainty that body armor of 600 micrometers in thickness made from six layers of 100 micrometer thick carbon nanotube yarns could reflect a bullet with an initial muzzle energy of 320 Joules [8]. To put this into perspective, an AK-47 fires rounds possessing roughly 2,000 Joules of kinetic energy. In order to reflect these deadly projectiles, a soldier's graphene nanotube composite armor would only have to be about 4 millimeters thick. This would result in an extremely lightweight armor that could stop most common infantry rounds without hindering the soldier's mobility.

METHODS OF PRODUCTION

While graphene may seem like the wonder material and capable of solving several problems that we face in the world, there are still many challenges to face with graphene. The largest problem faced today is in the production, where we have yet to develop a method for industries to produce sheets of the material on a large scale. Attempts at creating this super material include growth on materials such as silicon carbide, titanium carbide, nickel, copper, and other metals [3]. Another method of producing graphene is the micromechanical cleavage (MC) method, also known as the scotch tape method [3]. This involves using an adhesive tape to separate a material into two sheets. This procedure is possible because the bonds formed by the adhesive are stronger than those that hold together the layers of graphite [3]. This method was used to first form graphene in the lab [3]. However, the efficiency of such methods is extremely low and cause hesitation to be used as large scale production methods.

Graphite Separation and Exfoliation

The most promising source of graphene sheet production continues to be from a source of graphite, which is found in nature as a chunk of carbon. Graphite consists of a number of layers of graphene stacked on top of each other held together by the intermolecular van der Waals forces which are much weaker than the covalent bonds holding together the carbon rings in graphene [3]. Recently, scientists have found a way of separating these layers of graphene by dropping the graphite mineral into a specified solvent [9].

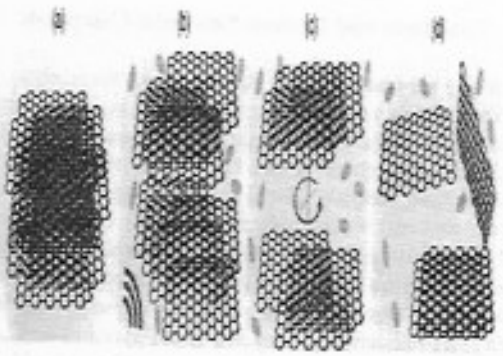


FIGURE 3 [10]
Exfoliation and Separation of Graphene from Graphite

The exfoliation process, which is shown in Figure 3, "typically involves three steps: (1) dispersion of graphite in a solvent, (2) exfoliation, and (3) purification" [9]. The molecules of the solvent separate the graphite into sheets due to the stronger interactions between solvent and graphene than graphene and graphene [9]. This process relies on the interactions between the carbon and the solvent which work to pull layers of graphene apart from each other, overcoming the natural intermolecular bonds. Then, exfoliation occurs by heating the solution and applying ultrasonic heat waves to it causing bubbles to form between solvent and graphene clearing off the excess solvent [9]. Lastly, to purify the graphene, it is left to sit to balance the attractive forces within each sheet where it can then be separated into longer individual sheets [9]. This process is a quick way of producing graphene in large sheets for mass production where most materials needed can be found in any laboratory.

The biggest concern with this method is that the typical solvents used in exfoliation such as N-methylpyrrolidone (NMP) and N-dimethylformamide (DMF) are typically very expensive and can be toxic [3]. NMP, for example, has been used in tests on rats to study its adverse effects. The California Department of Public Health concluded that NMP can lead to headaches, nausea, dizziness, and can cause abnormalities in babies who were exposed to NMP during pregnancy [11]. Since use of such chemicals can be damaging to life and the environment, scientists have looked for substitutes that can be used to replace these toxins such as acetone, ethanol, methanol, and acetonitrile [3]. However, when using such a solvent like ethanol, the yield of the reaction could not compare to the results obtained when using the toxic solvents. Graphene exfoliated from ethanol has a concentration of 0.04 mg/mL whereas NMP can produce graphene with a concentration of 0.90 mg/mL [3]. Attempts at using water as a solvent have also proved unsuccessful due to the hydrophobic nature of graphene causing it to repel the added water [3]. Other methods are currently being tested in order to make graphene production an environmentally safe and sustainable procedure.

Graphite Oxide

Another possible solution to mass production of graphene is the production of graphene oxide (GO). GO is analogous to graphene in its properties such as being one dimensional, extremely strong, and exceptionally conductive. GO is produced through the separation of graphite oxide, produced by the oxidation of graphite with a carbon to oxygen ratio of 2:1 or 3:1 [12]. Just like graphite, graphite oxide obtains a layered structure where GO layers are stacked on top of each other to make graphite oxide [12]. However, these GO layers contain oxygen "functional groups" which given graphite oxide special characteristics such as being hydrophilic and providing a larger gap between each layer of GO [12]. The oxygen found within the graphite oxide provides greater repulsion between the layers making the process of separation of GO from graphite oxide easier than graphene from graphite. The hydrophilic nature of graphite oxide, due to the presence of oxygen, allows for more methods of separating individual GO layers from the graphite oxide such as administering a thermal shock or placing the substance in a polar solvent [12].

At one point in time, many saw GO as a transitional stage for the production of graphene. However, graphene created from GO has been proven to be more difficult to make and more defective when produced [12]. While GO may not be an effective answer to the mass production of graphene, it is still important as it has most of the same properties. Like graphene, GO is a one-dimensional product that has similar characteristics of strength and conductivity. A single sheet of GO is about 1.4 nanometers thick making it 3 times thicker than a sheet of graphene [13]. While graphene from GO may be difficult to make and impure, GO does however hold dissimilar properties of its own which could be useful in applications where graphene is not a viable option [12].

COST AND EFFECTIVITY ANALYSIS

Cost

Due to the difficulty in producing large amounts of graphene effectively, the cost of making and selling graphene is extremely high. At the end of 2015, graphene could be bought for around $100 per gram [14] or about $60 per square inch [15]. This contrasts largely with the raw materials from which graphene is made such as graphite which sells on average 50 cents per gram, 200 times less than the price of graphene. Most of the world's graphite today comes from mines in China and India [14]. Using graphite from these countries so far seems to be the cheapest method for producing graphite, but it is very difficult to develop pure forms of graphene from graphite. When looking at other methods such as growth on metal plates, prices tend to rise drastically. The material needed for this process usually costs much more than graphite and other supplies needed to separate the graphite [14]. While these methods seem to produce pure graphene, they tend to grow at a low rate and at a high cost to the producer [14].

It is predicted that graphene prices will drastically decrease within the next ten years as production costs go down and effective large scale production methods are introduced [14]. As the possibility of mass production becomes a closer reality, interest in the material has skyrocketed. The European Union has invested $1.3 billion in graphene research while Samsung already has hundreds of patents on the material [14]. The graphene industry is booming and within the next ten years, graphene should become visible in many aspects of life [14].

Restrictions on Effectivity

As mentioned earlier, when put to the test, graphene provides a substantial amount of resistance when absorbing an impact. The material has been tested to be 200 times the strength of steel [15], can stop projectiles from piercing it at 3 km/s, and had a stopping power 10 times greater than that of steel [6]. Once layered on top of each other, sheets of graphene and graphene composites, can absorb extremely high amounts of energy only requiring 4 millimeters in thickness of either material to stop an AK-47 assault rifle bullet from piercing through the skin. Currently bulletproof vests are made of Kevlar which has the capability of stopping small caliber handguns and shotguns. However, to stop impact from an assault rifle such as an AK-47, metal or ceramic plates must be used on top of the vests which are impractical due to their rigidness.

While graphene may be a good substitute for such material, implementation of providing the military with graphene body armor does not seem viable until at least a couple of more years. Even if graphene was being produced in large quantities for a cheap cost, it would still take some time and a lot of money for the military to provide all of their units with this technology. The United States Military has made almost no mention of the possibility of graphene as a source of protection, but hopefully once the material becomes more easily produced and cost-effective, they will begin to see the practicality that it can be used for on the battlefield.

APPLICATIONS TO BULLETPROOFING

Adoption of Graphene Products in the Military

Even though graphene composite armor has not yet been adopted by military personnel, the concept is the focus of many researchers across the globe. Although the material has the potential to be used for a wide variety of purposes in the armed forces, for the purposes of this paper, the focus will remain on its applications to bulletproofing. Not only would the material be perfect for protecting the bodies of soldiers, but also for acting as a protective barrier on tanks, helicopters, and other combat vehicles. Its ballistic resistance properties have been proven on a small scale, and many military research companies

have been tasked to see if it can be applied to real-world combat. One of these many organizations is the United Kingdom's Defense Science and Technology Laboratory [16].

The British team of scientists plans to develop a rough image of ground warfare around the year 2030 through extensive research [16]. This involves surveying current military developers regarding their latest and upcoming developments, as well as instituting an open call for research submissions to be considered for the future, in order to monitor the progress being made behind closed doors [16]. After gathering countless plans for tomorrow's warfare, the British team concluded that neglecting the possibility of graphene armor would put their nation at a serious disadvantage on the global scale [16]. It is believed that the bulletproofing industry's main roadblock, the inability to mass produce the material, will soon be subverted, allowing military combat personnel to be outfitted with the composite vests [16]. After this problem is solved, the Defense Science and Technology Laboratory plans to work to make this possibility a reality [16].

In regard to the sustainability of this technology, it will prove invaluable in the quest to better protect the men and women of our armed services. Although the word "sustainability" usually refers to an entity's ability to preserve the environment, when it comes to the application of graphene to bulletproofing, the word is better representative of the capacity of the new vests to preserve lives. Having a strong and dependable military that can ensure the safety of everything and everyone within its borders is an essential aspect of any nation. This allows for the civilians to focus on bettering the world we live in without worrying about conflict.

Sadly though, the risks that military personnel face on a day to day basis are extreme and unyielding, and many brave men and women lay down their lives for their nation. As the number of casualties rises, it becomes harder and harder for a nation to maintain a strong military. Once soldiers are equipped with graphene vests, the death toll will evidently drop, dramatically increasing the sustainability of the armed forces of the world.

Potential Uses in Civilian Life

While graphene definitely has the possibility of enhancing technology in the military and making warfare safer for our troops, it also holds the opportunity to impact the life of everyday citizens. Graphene bulletproof vests can be important for people such as police officers, SWAT teams, bodyguards, and public figures such as the President of the United States. The strength and lightweight characteristics of graphene provide the wearer of these vests protection from bullets without the appearance of wearing one. They give the present-but-unseen sight which could be useful especially for public figures who do not want to distract their audience by wearing a giant bulletproof vest. Due to the flexibility of the material, there is even the possibility that someone could wear an entire suit made of graphene to protect areas of the body that would otherwise be exposed while wearing a vest.

Due to its strength and lightweight capacities, graphene also has the capability to affect other areas of life. The use of graphene as a composite material provides a very high strength to weight ratio allowing it to be useful in building structures that must be both strong and lightweight such as airplanes and windmills [17]. Its high electrical conductivity allows graphene to be implemented in airplanes where it can provide a coating along the exterior case to protect the plane from electrical damage when struck by lightning [18]. The strength and lightweight properties of this coating also provide a reinforced casing to protect from damage by larger objects without the added weight that another strong metal may offer.

In addition to the previously mentioned impacts on sustainability, graphene armor also promises to better the quality of life for many different types of people, exhibiting social sustainability. This subdivision of sustainability is defined as "the ability of a community to develop processes and structures which not only meet the needs of its current members but also support the ability of future members to maintain a healthy community", and this impenetrable armor allows for just that [19].

For example, a police officer equipped with a full-body graphene suit would be near untouchable by the small caliber weapons that are commonly used by criminals. This would better protect the courageous men and women of law enforcement, allowing them to more effectively carry out their duties, improving the lives of everyone. Another example is the better protection that the vests would offer a businessman who travels to dangerous parts of the world. Business ambassadors allow for international commerce, building the global economy. Such a position is essential in the world we live in, and eliminating the risk from the profession would better the quality of life for those who practice it. These benefits will carry into future generations, allowing for a society free of unnecessary death.

CONCLUSION

The most difficult aspect of producing a bulletproof material is that before the material is even implemented and used throughout the armed forces, armor piercing bullets and weapons are being designed to break through the new form of protection. There is nothing new about the concept of developing countermeasures in order to overcome an opponent's defense. History dictates that shortly after the successful mass production of graphene composite armored vests, advances will be made in the weapons industry in order to pierce them, just as modern day firearms are capable of piercing Kevlar protection. Although this throws the thought of graphene armor ending deaths due to warfare worldwide out the window, it represents the natural progression of military technology, and it will surely reduce the number of casualties and injuries after firefights in certain theatres of war. For example, the vests will give soldiers at war with less technologically advanced areas of the world an extreme edge

in combat, protecting completely against AK-47s and other weapons commonly used by underdeveloped nations.

Ultimately, regardless of advances in weaponry, graphene composite armor will better protect the vital organs of a soldier, greatly increasing his chances of survival if caught in a barrage of enemy fire. Shortly following technological advances that allow for the mass production of large sheets of graphene, it will almost certainly be adopted by the bulletproofing industries of technologically forward nations. Born in a laboratory at Rice University in Texas, the concept of using graphene to stop bullets has been proven effective through multiple case studies. Furthermore, it will soon be economically feasible, and will change warfare forever.

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