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Durable and flexible graphene composites based on artists' paint for conductive paper applications

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ABSTRACT

An acrylic emulsion artists' paint containing chlorinated copper phthalocyanine pigment was modified with variable-size multilayer graphene (exfoliated graphite) to induce low electrical resistance; composite films were spray-cast on common printing paper, heat-cured, and subsequently polished under mild compression, to produce highly conductive paper. The mechanically robust conductive paint showed excellent adhesion to the underlying paper, as determined by Taber abrasion and tape peel tests, which displayed no adhesive failure under the test conditions studied. The conductivity of the paper substrates were tuned by changing the concentration and the size of the multilayer graphene particles. Detailed conductivity measurements showed stable Ohmic current–voltage behavior. The optimum graphene-in-paint formulations resulted in sheet resistances of the order of 10 Ω/sq. Standard electrostatic force microscopy measurements showed uniform surface electric field gradient distribution strongly correlating with the surface topography. Similarly, scanning Kelvin probe microscopy measurements indicated stable work functions close to 5 eV, comparable to highly-ordered pyrolytic graphite. Furthermore, Kelvin probe measurements were more sensitive to surface charges related to copper phthalocyanine domains, which are known to have semiconducting properties. Finally, the conductive papers were also tested in the 0.50–0.75 terahertz frequency range for electromagnetic interference shielding (EMI) characterization and displayed quasi-metallic shielding performance.

1. Introduction

The demand for flexible and durable light-weight electronics has increased in recent decades due to the proliferation of new communications and sensor technologies, e-textiles, and the need for adaptable power storage. Conductive composites in paper-based and textile applications have been the subject of extensive research [1–6] for their applicability toward addressing this demand in future electronics. A generic and ubiquitous substrate, such as paper, offers a unique platform for the testing and low-cost implementation of new composite technologies; easily translating across multiple substrate platforms and industrial applications, such as photodiodes, smart fabrics, printable electronics, and

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soft-screens, among many others. As technologies advance, obsolete electronic detritus from years past now presents ethical and societal challenges related to its environmentally-benign disposal. It is thus desirable that future technologies be designed such that outdated equipment is easily broken down under natural conditions with low environmental impact. Flexible paper and textile electronics represent a solution to these nontrivial challenges, with the added benefit of a reduced bulk which is present in much of the current and previous technology; eventually taking up space in a landfill or, even worse, increasing pollution in the natural landscape. A composite, comprised of multilayer graphene (MLG) [7] in the form of exfoliated graphite in an acrylic artists' paint polymer matrix, is presented herein for conductive paper applications requiring a *light-weight and low-cost* solution, with the added benefits of *extreme durability, flexibility,* and *quasi-metallic electronic properties.*

Acrylic emulsion artists' paints were introduced in the 1950s and 1960s. Compared to oil-based paints, acrylic emulsion paints are capable of high pigment loading, forming coatings that can dry quickly and be thinned with water; they also have good clarity, excellent elasticity and high resistance to ultraviolet degradation [8,9]. Earlier paint formulations used copolymers of methyl methacrylate (MMA) and ethyl acrylate (EA) [10]. Today, the acrylic emulsion paints utilize poly (*n*-butyl acrylate/methyl methacrylate) copolymer dispersed in water. These films tend to be slightly tougher and more hydrophobic than the MMA/EA resins, making them more resistant to outdoor exposure. These emulsions offer advantages due to their unique interactions with paper surfaces after application, including efficient encapsulation of pigments to form a continuous film, absorption into the texture of the paper, and polymerization to form a robust film or painting, as schematically illustrated in Fig. 1 [11].

There are many different types of pigments used in acrylic emulsion paints as color sources. Among them, phthalocyanine green (CuPc), a complex of copper (II) with chlorinated phthalocyanine, has been widely used as a filler [12]. The chemical formula of this compound ranges from $C_{32}H_3Cl_{13}CuN_8$ to $C_{32}HCl_{15}CuN_8$, depending on the extent of chlorine substitution. Due to its stability, phthalo green is used in inks, coatings, and many plastics. The pigment is insoluble and has no tendency to migrate in the material. It is a standard pigment used in printing ink and in the packaging industry, as well as in many cosmetic products. Of interest, CuPc particles have recently been studied for use in quantum computing [13] and as a doping agent to enhance material properties in electrical and semiconductor systems [14], thus forming the rationale for choosing this specific pigment to create a novel conductive composite.

Long theorized [15], graphene has been a major focus of research efforts since its discovery in 2004 [16]; however, processing large sheets for commercial and industrial applications still remains cost-prohibitive. A cheaper, albeit less conductive, alternative to monolayer sheets of graphene is exfoliated graphite: an aggregate nanomaterial comprised of MLG with high aspect ratio that is relatively simple to manufacture in bulk for low cost. Monolayer graphene consists of a sheet of carbon atoms arranged in a hexagonal lattice, the structure of which gives rise to an inherent mechanical strength [17], as well as ballistic electron transport [18] through the covalently interlinked network. The attractive properties of graphene are numerous, yet generating defect-free and large-area graphene lattices necessary for realizing many of the desired attributes remains a challenge, and reproducibility is a concern. While electron scattering occurs readily due to the imperfect exfoliated graphite structures, the low electrical resistance of the graphene layers comprising the aggregate multilayer graphene particles enhances conductivity of the composite. A spray-cast MLG composite, in the form of exfoliated graphite dispersed in a pigmented acrylic artists' paint polymer matrix, possessing attributes approaching that of highly-ordered pyrolytic graphite is shown here to have potential for durable and flexible conductive paper applications, such as large-area flexible electronics and electromagnetic interference (EMI) shielding surface treatments without high monetary and environmental costs.

Approaches toward conductive papers and inks have been studied in the past [19–23], but many have required costly components, complicated fabrication procedures, or high energy expenditure to produce. As synthesis techniques improve, comparable inks and conductive colloidal suspensions are becoming cheaper, but often rely on ground-up development of compatible polymer binders. The novelty of the present approach relies on combining MLG with an *existing* polymer emulsion technology found in acrylic artists' paint to reduce costs, with the added benefit of a nano-pigment suspension for facilitating additional doping properties. For reasons of cost, high-performance composites containing precious metals, such as gold and silver, are economically

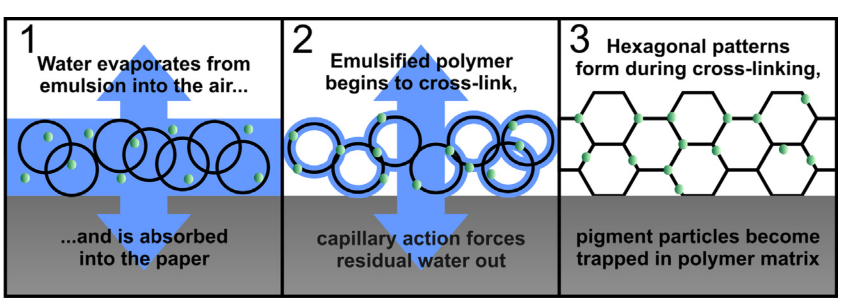

Fig. 1 – Application and setting of artists' acrylic emulsion paint (shown in blue) on a paper surface (in gray). Circles represent the polymer emulsion, which upon drying cross-links to form hexagonal bonds, thus acting as a matrix for pigment nanoparticles (shown as green dots). Based on the scheme reported in [11]. (A color version of this figure can be viewed online.)