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Infrared-transparent films based on conductive graphene network fabrics for electromagnetic shielding

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ABSTRACT

Transparency in the infrared (IR) light region and high conductivity for electromagnetic (EM) shielding performance are contradicting properties for conventional window materials. It is challenging to explore a new class of materials with both IR transmittance and high electrical conductivity. Herein, middle-IR transmittance and EM-shielding performance are realized by graphene network fabrics (GNFs). GNFs are fabricated by chemical vapor deposition using copper mesh with different geometric constructions as the sacrificial substrate. The structure of GNFs endows the as-fabricated material high IR transmittance, good electrical conductivity, and EM-shielding efficiency. The grid parameter τ with regard to the square aperture and wire width exerts a profound effect on the EM-shielding performance. The highest EM-shielding efficiency is 12.86 dB at 10 GHz with a transmittance of 70.85% at 4500 nm. Meanwhile, the highest IR light transmittance is 87.85% with an EM-shielding efficiency of 4 dB. Based on the experimental and theoretical analyses, the EM-shielding efficiency is prominently dependent on microwave absorption.

1. Introduction

Infrared (IR)-transparent windows have drawn tremendous attention due to their practical applications as sensor or detector components for military and civilian utilities [1]. There are two challenging requirements for these materials, such as high IR transmittance in order to guarantee the optical properties of IR sensors/detectors, as well as good electrical conductivity to ensure satisfactory electromagnetic (EM) shielding properties. Great efforts have been devoted to pursue highly transparent materials. Most reported IR-transparent window materials are electrically insulated, such as Ge, Si, MgO, Al_2O_3, and ZnS, which are not ideal candidates for application in the EM-shielding field [2]. Considering Drude's free electron theory, a high carrier concentration of transparent conducting oxide film results in a blue shift of the plasmon cutoff wavelength, thus leading to a contradiction between film conductivity and transparency in the IR region [3]. As transparent conducting oxide films, indium tin oxide (ITO) or ZnO shows excellent electrical conductivity

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due to the improvement of carrier concentration by doping. However, the reflection and poor transmittance for IR light did not fulfill the basic requirements of IR-transmittance window materials [4]. The exploration of new materials combining transmittance in the IR region with high conductivity for affording EM-shielding properties is highly desired. Graphene, a monolayer of sp^2-bonded carbon atoms, shows excellent conductivity and high light transmittance. Electrons moving in graphene behave as massless Dirac fermions, and they exhibit fascinating low-frequency electrical transport phenomena, which endow graphene IR transparency [5]. Moreover, large-area and high-quality graphene film with controlled layer number can be successfully prepared using the chemical vapor deposition (CVD) method. The resistance of graphene transparent film produced by the CVD method reached 150–770 $\Omega\,sq^{-1}$, and with 70–90% transmittance values in the visible region [6–8]. However, state-of-the-art graphene used in middle-IR-transparent conducting film has seldom been reported.

Meanwhile, tremendous efforts have also been made to enhance conductivity and EM-shielding performance. As is known, it is of great importance to shield the emission of EM radiation of electronic detectors, which can generate significant negative effects on our living environment, and laboratory and military applications. Up to date, traditional shielding materials, such as metal-based materials with high conductivity, suffer from stringent preparation conditions [9–11]. In order to solve the traditional material's drawbacks, great efforts have been dedicated to the polymer-based composites due to their superior features, such as light weight, resistance to corrosion, and good processability [12]. The EM-shielding efficiencies of these polymer-based composites mainly depend on the intrinsic conductivity, magnetic permeability, aspect ratio, and content of fillers [13,14]. However, the insulated polymers always impair the overall conductivity of the composites, and hence impede the performance of EM-shielding. Recently, carbon fibers, carbon nanotubes (CNTs), and chemically modified graphene have been used as conductive fillers, which can increase the electrical conductivity and connectivity of polymer-based composites [15–21]. For example, chemical reduction graphene oxide (RGO) and CNTs were applied to increase the EM-shielding performance of polymer composites [22,23]. To further reduce the density of carbon-based polymer composites, foam structures were designed and prepared, such as CNT–polystyrene (PS) composites foams with an EM-shielding effectiveness of 14 dB [23], CNT–epoxy composites with 23 dB [24], graphene/polymer microcellular foams with 15 dB [25], and graphene/polyetherimide (PEI) composites foams with 12 dB [26]. However, chemically modified graphene used in these methods is harmful to electrical conductivity due to the abundant defects including incomplete lattice and OH or COOH groups. As a result, Chen et al. developed a template-directed CVD method to fabricate flexible three-dimensional graphene/poly(dimethylsiloxane) (PDMS) foam structure, exhibiting an EM-shielding efficiency of 30 dB for a graphene content of <0.8 wt% [27]. It is worth noting that these solid or foam structures of carbon–polymer composites are nontransparent in the visible or IR light range.

Up to date, only few reports have focused on the development of transparent EM-shielding materials. For instance, the transparent stainless steel fiber/silicone resin composite was prepared by a blending shortcut method with a visible light transmittance of 67% and an EM-shielding effectiveness of 15–26 dB [28]. The transparent Ag nanowires (NWs)/poly(ethersulfones) (PES) film was fabricated by a two-step injection polyol method, exhibiting an EM-shielding efficiency of 25 dB with a transmittance of 81% in the visible–UV wavelength region [29]. However, AgNWs are found to be unstable due to the phase transformation of silver oxide species in air, and thus they lose their conductivity and relevant EM-shielding performance. PEI/RGO interleaved film was prepared by electrophoretic deposition with an EM-shielding effectiveness of 6.37 dB and an visible light transparency up to 62% [30]. The monolayer CVD graphene possessed a high transparence of 97% in the UV–visible wave band, but it only showed an average EM-shielding value of 2.27 dB [31]. Thus, it is still challenging to develop a facile strategy to enhance the EM-shielding efficiency as well as the transmittance in the IR region.

In this paper, we demonstrate middle-IR-transparent conductive graphene network fabrics (GNFs) with promising EM-shielding properties. GNFs are fabricated by the CVD method using copper mesh with different geometric dimensions as a sacrificial substrate [32]. We discuss the details of this material in the process of preparation and its performance in middle-IR transmittance, electrical conductivity, and EM-shielding efficiency. These properties are affected by the grid parameter τ, which can define the square aperture and wire width of this configuration. The highest EM-shielding efficiency is 12.86 dB at 10 GHz with a transmittance of 70.85% at 4500 nm. Meanwhile, the highest IR light transmittance is 87.85% with an EM-shielding efficiency of 4 dB. Based on the unique configuration and properties, we expect that the present strategy might be an important complementarity for traditional EM-shielding materials.

2. Experimental details

2.1. Materials

The copper mesh was purchased from Shanghai Temin Screening Co. Ltd. (Shanghai, China). Periodicity of the copper mesh samples is defined as mesh number based on the variation of the square aperture and wire width. The square aperture and wire width are 409 and 176 μm, 278 and 130 μm, 173 and 115 μm, and 108 and 90 μm for copper meshes of 40-, 60-, 80-, and 120-mesh size, respectively. Polymethyl methacrylate (PMMA) was obtained from Shanghai Jingchun Reagent Co. Ltd. (Shanghai, China). Its density and average molecular weight are 1.18 g/cm^3 and 95,000 g/mol, respectively.

2.2. Synthesis of GNFs

GNFs were first grown on copper meshes of different square apertures and wire widths by the CVD process. The copper meshes were immersed in acetic acid at 50 °C for 5 min, then cleaned with deionized water, and dried at 60 °C for 10 min in vacuum. The copper meshes were cut into dimensions of 1×1 or 2×2 cm^2, loaded into a fused silica tube, and heated to 1000 °C under H_2:Ar = 30:50 sccm (standard-state cubic centimeter per minute) flow for 20 min to remove the surface