

Massive Electrical Conductivity Enhancement of Multilayer Graphene/Polystyrene Composites Using a Nonconductive Filler

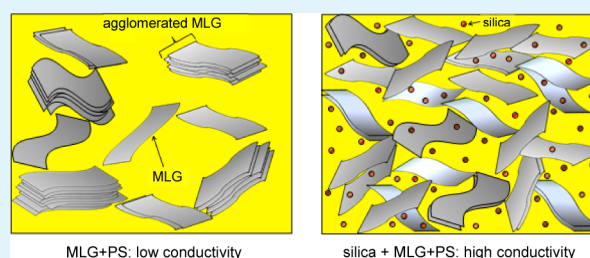
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ABSTRACT: We report a massive increase in the electrical conductivity of a multilayer graphene (MLG)/polystyrene composite following the addition of nonconducting silica nanoparticles. The nonconducting filler acts as a highly effective dispersion aid, preventing the sheetlike MLG from restacking or agglomerating during the solvent casting process used to fabricate the composite. The enhanced dispersion of the MLG leads to orders of magnitude enhancement in electrical conductivity compared to samples without this filler.

KEYWORDS: multilayer graphene, electrical conductivity, polymer, composites, dispersion



Defect-free single layer graphene sheets consist of single-atom-thick, sp²-bonded, hexagonally arranged carbon

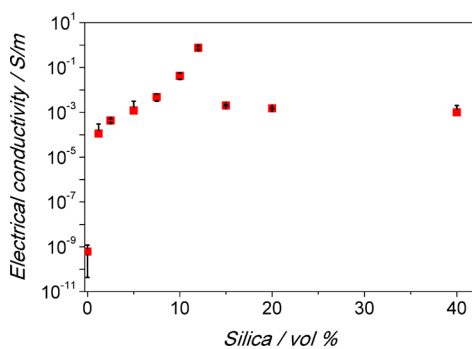


Figure 1. Electrical conductivity of MLG-silica-polystyrene composites at 2.5 vol % MLG. The conductivity increases by several orders of magnitude as 200 nm silica particles are added.

atoms. They display remarkable properties including exceptional in-plane electrical and thermal conductivity, high stiffness and tensile strength, optical transparency, negligible permeability to gases, and van der Waals transparency.^{1–8} The scientific and commercial interest in graphene is not restricted to the pristine monolayer, but includes related 2D materials that include few-layer graphene (FLG), multilayer graphene (MLG), and chemically modified forms such as graphene oxide (GO).² The essentially two-dimensional nature of these materials along with their excellent properties makes them important as fillers, imparting useful functionalities into matrices. Polymers that display high conductivity have a variety of uses ranging from bulk applications such as antistatic mats

and fuel lines,^{9–15} to specialty applications such as radiation shields, sensors, and electrodes for batteries.^{16–24} Although single-layer graphene remains expensive and best suited for high-value applications in electronic devices, optoelectronics, and supercapacitors,^{1,25} the much lower cost MLG is a more promising material for applications that seek to impart electrical conductivity to polymers. Therefore, we target MLG/polymer composites in an effort to provide electrical conductivity to the insulating polymer. In this paper, we report an unexpected result, where we observe a massive enhancement in the electrical conductivity of a MLG/polystyrene composite upon the addition of a second, nonconducting filler.

To achieve practical levels of electrical conductivity in an insulating material, a conducting filler must be loaded to a volume fraction beyond the percolation threshold.^{16,17} MLG are two-dimensional structures, which if allowed to rotate freely in a matrix, sweep a “volume” that is a sphere of diameter corresponding to the lateral dimensions of the MLG, giving a theoretical volume loading at percolation that is well below that of spheres.¹⁷ If MLG are modeled as ideally dispersed and randomly rotated disks of aspect ratio AR (AR = disk diameter/thickness), the percolation threshold ϕ_c is given by²⁶

$$\phi_c = 1.5(\phi_{\text{sphere}}/\text{AR}) \quad (1)$$

In eq 1, ϕ_{sphere} is the percolation threshold for spheres, i.e., $\phi_{\text{sphere}} = 0.29$ ($\phi_{\text{sphere}} = 0.29$ is for monodispersed spheres; that number is lower if there is polydispersity, but remains of the

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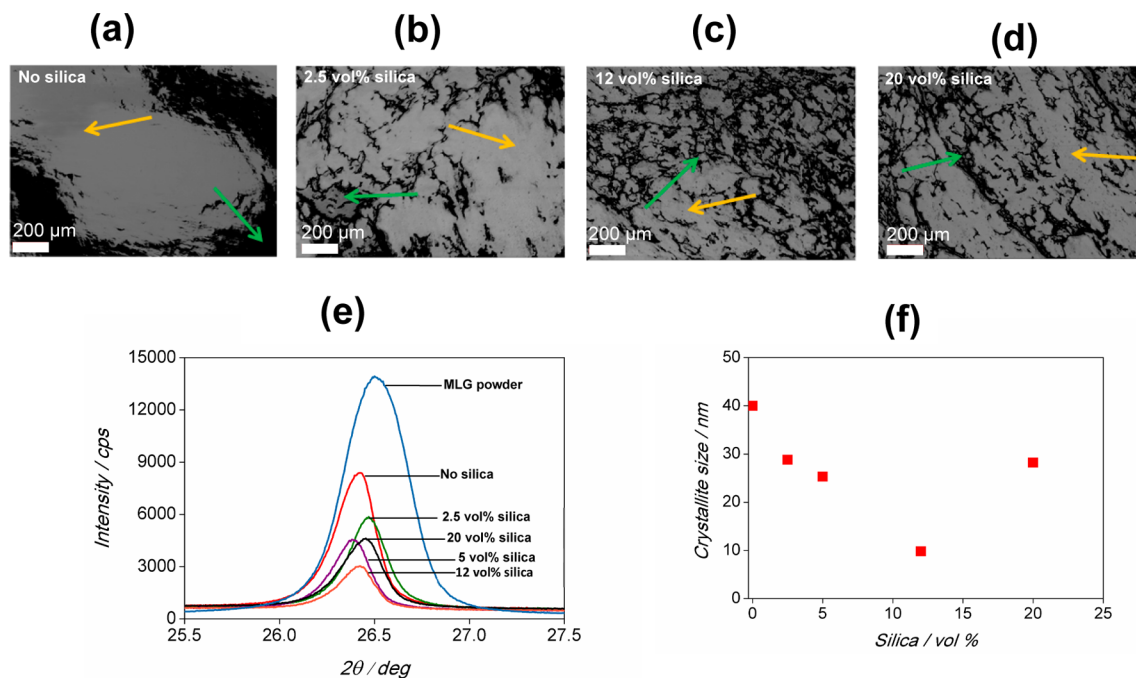


Figure 2. Backscattered SEM images showing the distribution of MLG in the polystyrene matrix. (a) No silica. The dark regions show agglomerated MLG sheets. (b) 2.5 vol % silica. The MLG dispersion is improved. (c) 12 vol % silica. The dispersion of MLG is improved over cases a and b. (d) 20 vol % silica. The dispersion of MLG deteriorates because of the presence of excess nonconducting silica. Yellow arrows, polystyrene; green arrows, MLG. The silica particles are not visible at this magnification. (e) X-ray diffraction plots around the graphite (0 0 2) peaks for all samples. (f) Average crystal dimension of MLG agglomerates obtained using Scherrer's equation. The crystal dimension decreases as silica is added, indicating improved dispersion and reduced restacking of MLG. At silica loading above 12 vol %, the crystal dimension increases again, indicating enhanced agglomeration or restacking.

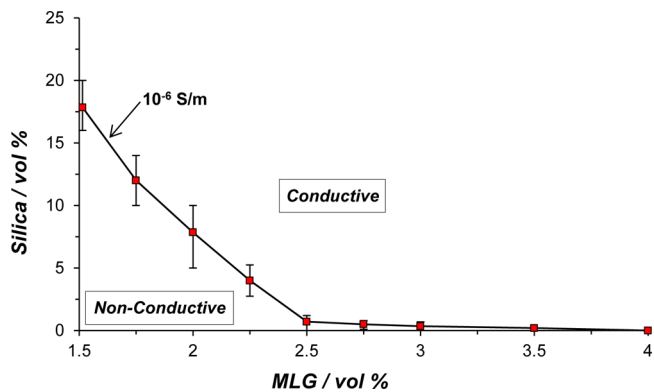


Figure 3. Partition between nonconductive and conductive regions of the MLG-silica-PS ternary composites at different loadings of MLG and silica nanoparticles. The data mark a (arbitrary) transition point from nonconductive to conductive at 1×10^{-6} S/m, and the line is drawn to guide the eye.

same order of magnitude). Because AR can take on values of the order of 10^4 for MLG, the advantage of using these high aspect ratio conducting particles in lowering the volume loading at percolation becomes apparent. Providing such a low loading at percolation also has a significant benefit for mechanical properties, particularly under impact conditions, as filler materials can act as nucleation sites for crack growth.^{27–29}

Although the volume loading at percolation is small for sheetlike materials, van der Waals attraction between these sheets causes rapid agglomeration, degrades dispersion, and enhances restacking. The restacking reduces the aspect ratio and typically prevents achieving the performance predicted by eq 1. Thus, dispersing these high aspect ratio sheets in a

polymer remains a major challenge. We hypothesized that the addition of a second filler could overcome this issue, because this filler would act as spacers and prevent agglomeration of MLG during processing. In addition, if the second fillers were dispersed homogeneously throughout the polymer, they would guide the sheetlike MLG into a more random orientation in the polymer, enhancing the probability of MLG percolation at low loadings.

MLG are purchased from XG Sciences, USA. The lateral dimension of these nanoplatelets is $\sim 25 \mu\text{m}$ and thickness is approximately 6 nm. 200 nm silica nanoparticles are purchased from Nyacol, USA. Polystyrene (MW 121 000) pellets are purchased from Styrolution, USA.

Seven grams of the polystyrene pellets are dissolved in 42 mL of N,N-dimethylformamide (DMF) and the solution is stirred magnetically for 12 h.³⁰ The silica particles are then added and the mixture is sonicated for 1.5 h. MLG at a concentration of 0.001 gm/ml are dispersed in DMF and sonicated for 1.5 h. Both particle-containing suspensions are then mixed in a 1:1 ratio and magnetically stirred for 2 h. This mixed suspension is then poured into methanol, an antisolvent for PS. The PS precipitates rapidly, creating the composite. The excess methanol is withdrawn, and the composite is dried in an oven for 18 h at 90 °C. The sample is then hot pressed at 120 °C to get rid of all entrapped air bubbles, and to create a sample with a disk-like shape that is amenable for electrical conductivity measurements. All reported loadings are based upon the volume percent in the final composite.

The surfaces of specimens are coated with silver paint to reduce contact resistance. A standard two-point probe using a constant current source (Keithley Instruments model 6221) is used to obtain bulk volumetric electrical conductivity. The

voltage drop across the specimen is recorded, and the resistance of the sample is calculated from this measurement. This is normalized with the dimensions of the sample to produce the electrical conductivity. The surface morphology of the composites is observed using scanning electron microscopy (Zeiss SIGMA VP FE-SEM) in backscatter mode. A Rigaku Ultima IV diffractometer with Cu $K\alpha$ radiation is used for the X-ray diffraction (XRD) measurements.

We added 200 nm diameter spherical silica particles to MLG-containing polystyrene, and show results for 2.5 vol % loading of MLG in Figure 1. The electrical conductivity of MLG-silica-polystyrene composites increases by several orders of magnitude as the loading of the nonconductive silica is increased. We rationalize this surprising observation by imaging the samples at various silica concentrations using scanning electron microscopy, and complementing those results with X-ray diffraction.

Figure 2a is a backscattered SEM image of the sample with no silica. The MLG are agglomerated rather than well dispersed in the polystyrene (PS), and the conductivity is 1×10^{-9} S/m. At 2.5 vol % silica, the conductivity of the composite rises dramatically to 10^{-4} S/m. Figure 2b shows better dispersion of the MLG at this silica concentration. As the silica loading is increased to 12 vol %, the conductivity rises further to 1 S/m, and the MLG are dispersed more uniformly throughout the sample (Figure 2c). Beyond 12 vol % silica, there is a decrease in electrical conductivity of the composite, which is then nearly constant over the remaining range of feasible silica loadings. The excess silica particles at these concentrations start to break the connectivity of the MLG network, as seen in Figure 2d at 20 vol % silica.

We measure the full width at half-maximum of the graphite (0 0 2) diffraction peaks (Figure 2e), and use Scherrer's analysis to determine an average "crystallite" size for the MLG as an indicator of restacking (Figure 2h). The average crystallite size decreases as the silica loading goes to 12 vol %, and then rises again. This indicates a suppression of restacking and also suggests improved dispersion of the MLG at concentrations up to 12 vol % silica, followed by increased MLG agglomeration as the silica content is increased further.

We use 1×10^{-6} S/m as a threshold value for determining if a sample is conducting, and summarize our data for a range of MLG and silica loadings in Figure 3. We show that adding a nonconducting (silica) filler can trigger conductivity in an otherwise nonconducting MLG/PS composite. That is, addition of a nonconductive filler can significantly reduce the loading of MLG required for percolation. While we have used 200 nm silica particles as dispersion aids in this work, we recognize that there is a range of materials, morphologies and sizes of fillers that can be exploited to impart desirable properties to a composite. Optimization of this novel second-filler concept will be the subject of future work.

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Notes

The authors declare no competing financial interest.

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