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Single-step self-assembly of multilayer graphene based dielectric nanostructures

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ABSTRACT

We present high performance multilayer organic/inorganic nanostructured dielectric films including well dispersed chemically modified graphene (CMG) charge polarization layers based on single step solution self-assembly. Multilayer film structures of alternating aluminosilicate and amphiphilic block copolymer (BCP) lamellar layers intercalated with CMG in the hydrophilic aluminosilicate domains are prepared by simple solution casting process. The resultant composite dielectric film attains a high dielectric constant (~30) along with low dielectric loss (<0.3). The increase of dielectric constant originates from the space charge polarization effect by high aspect ratio CMG, which is also precisely adjustable with the CMG composition in the composite films. Significantly, the dielectric loss rarely increased even with the injection of a large amount of conductive CMG fillers, as CMG plates are exclusively distributed in the hydrophilic lamellar domains without forming conductive connection in the film normal direction across hydrophobic domains. The composite dielectric film also demonstrates mechanically flexible and highly stable features while deposited on conventional flexible PEN substrates.

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Introduction

Complex material design based on nanoscale composite structures may offer efficient routes to the synergistic improvement of mechanical [1,2], electrical [2–4] and optical properties [5,6], which are hardly obtainable by single component materials. Various approaches to control the spatial arrangement of nanoscale components and adjust the chemical or physical interactions among the mixed components have been proposed so far [7]. One of the interesting features is ordered nanoscale composite system with regular and periodic spatial arrangements of different components [8,9]. This material design is generally considered to be able to offer the delicate control of diverse material properties over a wide range. In this context, the block copolymers (BCPs) are interesting structure directing self-assembly materials for the advanced nanocomposite structures, as the microphase separation of BCPs may provide highly periodic ordered nanostructures consisting of nanoscale spheres, cylinders, lamellae [10–12], which have been widely exploited for photonic [13,14] and electronic [15–17] applications.

Chemically modified graphene (CMG), which is commonly generated from graphene oxide (GO), is an intriguing material possessing widely controllable chemical and physical properties particularly depending on its reduction process. A notable advantage of CMG for composite process stems from the good dispersibility of GO in various solvents [18]. To date, CMG nanocomposites based GO have been extensively investigated for the enhancement of mechanical, electrical and optical properties [19–22]. Recently, CMG has also been employed as a conductive filler in dielectric materials. Dielectric constant, which is crucial index for the regulation of electrical interaction between the electric components, can be effectively increased by incorporating conductive filler.

When a voltage is applied to dielectric/conductive filler composite structure, dielectric charge carriers can be electrically driven and some of charges adjacent to conductive filler are accumulated in the conduction band of the filler. Meanwhile, the adjacent dielectric can be turned into the opposite space charge type to retain electroneutrality. Consequently, local polarization is built up in the composite structure and contributes to the increase of dielectric constant. In this regard, the dielectric/conductive filler composites with various structural designs have been researched, such as randomly mixed bulk heterostructures [23–27], solution-processed stacking layer structures [28,29] and conductive filler interlayered dielectric structures based on graphene transfer [30].

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In this work, ordered nanoscale composites of aluminosilicate, BCPs and CMG are introduced for the realization of flexible dielectric composite materials with high dielectric constant as well as low dielectric loss. The dielectric constant is increased by the highly selective intercalation of CMG platelets in the ordered aluminosilicate/BCPs films. The amount of intercalated CMG enables a wide range control of dielectric constant, which is dominated by the space charge polarization by CMG. Also, lamellae BCP self-assembly with surface parallel orientation hinders the out-of-plane arrangement of CMG platelets. This efficiently blocks the formation of conduction path through the film normal direction [23] and thereby minimizes the dielectric loss. Concurrently, mechanical flexibility of composite films is offered by organic part of BCPs, which enables structural robustness while maintaining a stable dielectric constant during the bending test over 500 times and repetitive measurements over 10,000 times.

Materials and methods

Materials

Aluminosilicate was synthesized by sol–gel reaction. GPTMS (Sigma-Aldrich) and Al(OBus)₃ (Sigma-Aldrich) were mixed with molar ratio of 4.28:1 and stirred for 1 h in ice bath. Then, 20 μ l of 3% Hydrogen chloride solution (37% Hydrogen chloride purchased by Sigma-Aldrich and diluted with deionized water) was added in the mixture. After 15 min, identical solution of 90 μ l was additionally blended and kept the solution with strong stirring at room temperature for 1 h. The resultant aluminosilicate solution consisted of small gel particles. CMG was formed from GO aqueous solution, following a modified Hummers method [31,32]. GO was dissolved in the mixture solvent of ethanol (anhydrous, Sigma-Aldrich) and deionized water with 9:1 vol ratio. As a structure directing agent, polystyrene-block-poly(ethylene oxide) (PS-*b*-PEO) (19 kg mol⁻¹-*b*-6.5 kg mol⁻¹, Polymer Source Inc.) was used and dissolved in toluene (anhydrous, 99.8%, Sigma-Aldrich) with 5 wt%.

Synthesis of composite solutions

Aluminosilicate solution

Aluminosilicate synthesized by sol–gel reaction was diluted in ethanol for the uniform thin film formation. Typically, 15 wt% aluminosilicate solution was used to form thin films with \sim 200 nm thickness.

Aluminosilicate/BCP composite solution

For ordered organic/inorganic lamellar nanostructure formation, BCPs were blended with aluminosilicate. PS-*b*-PEO BCPs were employed because the hydrophilic PEO block having a high compatibility with aluminosilicate enables this hybrid assembly. Blending ratio of aluminosilicate to BCPs ranged from 1:3 to 1:10.

Aluminosilicate/CMG composite solution

For the formation of CMG intercalated aluminosilicate film, aluminosilicate was first mixed with GO aqueous solution. For the reduction of CMG from GO, thermal annealing was performed after the solution casting of thin films. Based on the control of GO concentration in the mixture solution, composition of CMG in the composite film was determined.

Aluminosilicate/BCP/CMG composite solution

The multicomponent solution consisting of aluminosilicate/BCP/CMG was prepared by mixing the three components in the controlled sequence (Fig. S1). Aluminosilicate and BCP with the

weight ratio of 1 to 7 were firstly mixed, and then GO solution with various concentration was added. After thorough stirring of the mixture solution, composite film was spin casted on a target substrate. Similar with aluminosilicate/CMG composite film, CMG was obtained from the thermal reduction of GO, whose concentration in the solution determined the composition in the film.

Device fabrication

For the measurement of dielectric constant and loss of each composite film, parallel electrode system was used. A composite solution was spin casted on ITO bottom electrode to form a film of 200–300 nm thickness. After thermal annealing of each sample at 250 °C for 12 h, top electrode with Cr (3 nm)/Au (20 nm) was deposited on the composite films by e-beam evaporation.

Characterization

Nanoscale morphology of dielectric composite films was characterized using scanning electron microscopy (SEM, Hitachi S-4800) and atomic force microscopy (AFM, Bruker Multimode 8). For the quantitative analysis of CMG composition in a composite film, optical transmittance was measured by UV–vis spectrophotometer (Shimadzu, UV-2600). Dielectric properties were measured by electrochemical station (Bio-Logic SP-200). For the measurement of dielectric constant and loss, AC impedance measurement was performed in the frequency range from 10 Hz to 7 MHz with an applied voltage of 0.1 V. Dielectric properties were calculated from the impedance spectroscopy results.

Results and discussion

Self-assembly of multilayered dielectric nanocomposite films

Fig. 1(a) schematically presents the fabrication process for multilayered dielectric composite film consisting of aluminosilicate/BCP/CMG by simple single-step solution process. We firstly tested the composite solution of BCPs and aluminosilicate. Considering the effective swelling of PEO block by aluminosilicate mediated by hydrogen bonding, cylindrical PS-*b*-PEO (19 kg mol⁻¹-*b*-6.5 kg mol⁻¹) was selected for the lamellar film formation. After testing various blending ratios, the solution with the blending (weight) ratio (aluminosilicate: BCPs) from 1:6 to 1:8 was confirmed to form the lamellar structures (Fig. S3). In particular, at 1:7 blending ratio, the multilayered lamellar film was stably formed with a lamellar period of 20 nm. It is quite noteworthy that such a well-defined hybrid self-assembled nanostructure with alternating layers of organic and inorganic material can be readily formed by single-step solution casting.

For the selective intercalation of CMG flakes in the hydrophilic lamellar nanodomains of multilayered film, finely dispersed GO aqueous solution was mixed with BCP/aluminosilicate solution. In this step, the blending sequence of three components is highly important to avoid the unnecessary GO segregation. Due to the solubility difference of three components, the composite film blended in different mixing sequence revealed entire different morphology. In Fig. S4, mixing order of blue arrow leads to a well-dispersed composite film without any aggregation, while red arrow leads to a poorly defined morphology. In the order of blue arrow (Fig. S4(a)), aluminosilicate, which is well miscible with both BCP and GO solutions plays a role as a surfactant in the composite solution. As shown in Fig. 1(b), aluminosilicates chemically bonded with PEO blocks of BCPs preferentially interact with the oxygen group of GO and thus stabilizes GO flakes, showing a uniform dispersibility in the ethanol/water mixture. In addition, surface

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