



In situ reduction of graphene oxide nanoplatelet during spark plasma sintering of a silica matrix composite

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Abstract

Well dispersed silica-graphene nanoplatelet (GNP) and silica-graphene oxide nanoplatelet (GONP) composites were fabricated by optimising their processing conditions. Different processing methods, including colloidal and powder processing, were investigated using different solvents. High temperature and inert environment during SPS resulted in the reduction of the GONP during sintering. The in situ reduction of GONP in the SPS was investigated for various sintering times and temperatures, and characterised using Raman spectroscopy and XRD analysis. The composite sintered at 1200 °C, 50 MPa pressure and 15 min dwell time confirmed the recovery of the crystalline graphitic phase of GNP after reduction without crystallising the silica matrix. GONP was found to inhibit the crystallisation of the silica matrix at higher sintering times and temperatures possibly due to increased viscosity and reduced mobility of the silica particles bound to GNP.

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1. Introduction

Graphene has remarkable thermal,¹ electrical² and mechanical³ properties. It is being considered as a multifunctional nano-filler in composites for a wide range of potential applications. The vast majority of work in the last decade has focused on polymer–graphene composites, e.g., Refs. 4–11 and much fewer investigations have considered inorganic matrices, e.g., Refs. 12 and 13.

A considerable amount of work has been published on CNT reinforced inorganic matrix composites,^{14–19} but their applications are still very limited. The major difficulties associated with producing CNT based composite systems are: (1) CNTs tend to agglomerate unless they are surface functionalised²⁰; (2) CNTs are potentially toxic²¹ because of the presence of undesired metal catalyst as well as their nano-size. Graphene on the

other hand is easier to produce and disperse even without surface functionalisation.^{22,23} It is less toxic than CNTs because of its two-dimensional geometry (in the range of a few microns) and the absence of nano-sized catalyst.

Recently authors have reported improvements in the structural and functional properties of inorganic matrix composites with the addition of GNP/GONP. For example, Walker et al.²⁴ reported an increase of 235% in the fracture toughness of silicon nitride–GNP composites. Recently Porwal et al.¹² reported an improvement of 40% in the fracture toughness of alumina–GNP composites and a change in mechanism of crack propagation from inter-granular to trans-granular with the addition of GNP. Miranzo et al.²⁵ reported an increase of 100% in the thermal conductivity of silicon nitride–GNP composites. Fan et al.²⁶ reported a percolation threshold of 0.38 vol% and electrical conductivity of 1000 S/m for alumina–GNP (2.35 vol%) composites. In a review on graphene reinforced ceramic matrix composites,¹³ various synthesis routes for producing good quality GNP/GONP and ceramic nano-composites were discussed and the resulting properties of the composite materials were analysed. It should be noted that the reinforcement of inorganic matrix composites with the addition of GNP/GONP mainly

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depends on three factors: (1) amount of GNP/GONP loading; (2) interface between GNP/GONP and inorganic matrix; and (3) quality of GNP/GONP and its dispersion in inorganic matrix. The presence of GNP/GONP in inorganic matrix composites might dramatically affect many properties such as coefficient of friction, wear resistance,²⁷ coefficient of thermal expansion and thermal shock resistance. In view of these potential advantages along with the intrinsic properties of the inorganic materials such as high temperature stability, light weight and high corrosion resistance, inorganic–GNP/GONP composites are potentially attractive for a variety of applications.

So far the improvement in the properties of graphene nano-composites has been limited because of the difficulty in producing single layer graphene flakes. The strong van der Waals forces between graphene layers leads to GNP formation when using liquid phase exfoliation or milling methods. On the other hand these forces can be overcome by oxidising the graphene which avoids re-agglomeration of graphene flakes but in turn compromises its excellent electrical properties. Oxidised graphene is easy to disperse in aqueous solvents and can be used to produce GONP reinforced glass/ceramic composites. Authors have reported reduction of GONP either by using chemical or thermal methods.^{28,29} Spark plasma sintering (SPS) uses pulsed direct current in an inert/vacuum environment to achieve very high heating rates, thus reaching the sintering temperatures in just a few minutes. The inert and high temperature conditions in SPS are sufficient for reducing GONP to GNP during sintering.

In the present work, the processing conditions for preparing well dispersed silica-GNP/GONP composites are discussed. Colloidal and powder processing routes were investigated with different solvents including ethanol, deionised (DI) water, *n*-methyl pyrrolidone (NMP) and di-methyl formamide (DMF). SPS was used to consolidate the powders. SPS avoided any damage/decomposition of GNP/GONP by minimising the sintering times and reduced GONP to GNP during sintering. In situ reduction of GONP in SPS was investigated for various sintering times and temperatures using Raman spectroscopy and XRD analysis. Finally, the conditions for preparing well dispersed and reduced silica-GONP composites were optimised avoiding crystallisation of the nano-composites.

2. Materials and methods

2.1. GNP/GONP

GNP was synthesised using the liquid phase exfoliation method described elsewhere.^{12,30} Briefly, graphite flakes (Sigma Aldrich) were dispersed in NMP and sonicated (CV33 flat probe sonic tip, 50 W, 25 kHz) for 20 h in an ice cooled bath. After sonication, the suspension was centrifuged (Centurion Scientific) at 500 rpm for 45 min to separate the un-exfoliated graphite. The prepared GNP suspension was very stable with a yield of 4–8 wt%. The GNP was characterised using TEM (JEOL JSM-2010, 200 kV), Raman (633 nm Nicolet Almega XR-dispersive Raman) and UV–Vis spectroscopy (Perkin Elmer-Lambda 950).^{12,31} To prepare suspensions of GNP in the solvent DMF, already prepared GNP–NMP suspension was filtered using a

vacuum filtration unit and re-dispersed in DMF and sonicated for 20 min. It is possible to prepare GNP dispersions using liquid phase exfoliation because the energy required to exfoliate GNP is mainly balanced by solvent–GNP interactions. In the case of NMP and DMF, the surface energy of GNP matches that of the solvent which allows better exfoliation and improved stability of the GNP dispersions.^{32,33} For comparison, commercially available GONP powder (Nano-Innova) was used to produce GONP suspensions in DI water and ethanol. Known amounts of GONP were added to the above solvents and sonicated for 4 h using an ultrasonic bath (Branson-5510). DI water and ethanol were chosen as the processing solvents because of the good affinity of GONP to these solvents. It should be noted that the final concentration of both GNP and GONP suspensions were 1 mg/ml.

2.2. Processing methods

In order to optimise the conditions for preparing well dispersed and homogeneous powder mixtures of silica-GNP/GONP two different processing methods were investigated, colloidal and powder processing using different solvents. Because of the substantial difference in their surface chemistry, both GNP and GONP were expected to behave differently in the silica matrix. Also, different loading of GNP and GONP was attempted in order to understand the effect of concentration on the processing of these composites.

2.2.1. Colloidal processing

To prepare the silica-GNP and silica-GONP composite powders using a colloidal processing route, silica powder was added to different solvents including ethanol, DI water and DMF and sonicated for 2 h. The concentration of silica suspension was 20 mg/ml. Previously prepared GONP–ethanol, GONP–DI water and GNP–DMF suspensions were added dropwise to the silica suspensions while the mixture was magnetically stirred (200 rpm). After 2 h of magnetic stirring the suspensions were dried on a hot plate at 80 °C for 12 h. The dried mixture was ground and sieved using a 250 mesh sieve followed by drying in oven at 80 °C for 2 days.

2.2.2. Powder processing

Commercially available silica powder (Sigma Aldrich, 20 nm, 4 g) was added to previously prepared GNP–NMP suspension (1 mg/ml) and the slurry was ball milled at 350 rpm using a QM planetary ball mill (Nanjing University Instrument Plant) with zirconia balls (diameter – 10 mm) for 4 h with a powder-to-ball weight ratio of 1:20. After milling, the prepared slurry was dried on a hot plate at 200 °C for 4 h. The dried mixture was ground and sieved using a 250 mesh sieve.

2.3. Sintering and characterisation

The silica-GNP and silica-GONP composite powders were densified using a SPS furnace (HPD 25/1, FCT Systems, Germany, Furnace) at 1200 °C (heating, cooling rate 100 and 50 °C/min, respectively) under application of 50 MPa pressure

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