



Facile sol–gel synthesis of reduced graphene oxide/silica nanocomposites



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ABSTRACT

Novel silica-containing nanocomposites with a controlled carbon phase based on high quality reduced graphene oxide (rGO) were prepared via a cheap and facile sol–gel method, followed by pyrolysis in inert gas atmosphere. The resulting nanocomposite materials have an intimate bonding between rGO of low defect density and a partially crystalline silica matrix, as shown by Raman, FTIR and HRTEM studies. This processing route allows a straight-forward control of the content of the carbon phase and an excellent dispersion thereof within the silica matrix.

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1. Introduction

Polymer-derived ceramics (PDCs) route offers the possibility to synthesize novel ternary ceramic systems of different composition and microstructures by the controlled thermolysis of suitable precursors with a variety of chemical structures. An important class of ternary PDCs is represented by silicon oxycarbide (SiOC) ceramics. This class has attracted a lot of attention in the past 40 years due to its excellent resistance to crystallization and creep deformation at high temperatures as well as its facile synthesis [1]. Usually, polysiloxane polymers have been used as precursors for SiOC ceramics [1], which are amorphous, glassy materials consisting of mixed-bonds $\text{SiO}_x\text{C}_{4-x}$ tetrahedra and some amount of segregated carbon (or free carbon). The free carbon phase was derived from the thermolysis of organic substituents bonded at silicon in the polymer state. This microstructure was extensively investigated during the years and several microstructural models were proposed [2]. A special attention was offered to the free carbon phase, which was found to strongly influence the thermal stability against crystallization and decomposition of these ceram-

ics, as well as their functional and mechanical properties. It was found that the carbon phase is composed of randomly oriented fine graphene layers in a matrix of amorphous SiOC. It was postulated that the orientation, concentration as well as interface bonding of this graphene phase with the matrix should be the key for understanding the exceptional properties of this class of ceramics [1,2]. Thus, PDCs are intrinsically complex nanostructured systems, which may undertake significant microstructural changes when exposed to high temperatures. Simple model systems such as the graphene/silica nanocomposites in the present study can help to understand the structure and the interface bonding in silicon oxycarbides, features which are controlled by the concentration and dispersion of the carbon phase in the ceramic matrix. However, one should mention that the model system presented in this work has also some limitations. Thus, the prepared monolithic rGO/silica samples were hot-pressed at high temperatures (i.e., 1600 °C) and consequently showed some crystallization of the silica phase. This is not the case for silicon oxycarbides, which were shown to keep their amorphous nature up to their decomposition temperature. Nevertheless, the rGO/silica samples presented in this work are considered to exhibit one main common feature with single-phase and phase-separated silicon oxycarbides, i.e., the fate of the carbon phase and its bonding to the matrix.

Ever since first synthesized [3], the two-dimensional nature [4] and the exceptional electronic [5–13] and mechanical properties [11] of graphene have gained a lot of interest. As pristine

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graphene sheets with large lateral dimensions are insoluble in all common solvents [14], graphene oxide (GO) is the material of choice for the preparation of nanocomposites containing well dispersed graphene. GO contains reactive groups as carboxyl, hydroxyl and ketone groups at the edges as well as hydroxy and epoxy groups within the plane [15,11,16,17]. The presence of hydroxy groups in GO offers the possibility to disperse it in water and for using GO for example in condensation reactions [17]. This feature makes GO an interesting and suitable precursor for sol–gel reactions in aqueous media. The electrical conductivity of GO is relatively low and relies on the disruption of the π -network. This issue can be partially solved via chemical [13,18–20] (e.g., upon exposure to hydrazine monohydrate [19,12]), or thermal reduction processes [21–23].

The functional groups in GO were previously used to synthesize polymer nanocomposites composed of graphene and silica [24–27,5,28–30] or silicone matrices [31,32]. Usually, an appropriate functionalization of GO was performed in a first step [6,7,18,33–35].

In order to study the effect of the segregated carbon phase (i.e., content, organization, interfaces etc.), novel model systems for assessing the bonding of the carbon phase in SiOC ceramics were produced upon the pyrolysis of highly cross-linked gels composed of single-/few-layer reduced graphene oxide and silica. The gelation of rGO with TMOS offers the possibility to incorporate the graphene phase in a controlled way in the silica matrix. No supplemental chemical functionalization of the GO phase was necessary to provide good homogeneity of the nanocomposites. After pyrolysis of obtained gels containing different concentrations of graphene oxide, nanocomposite materials consisting of a high-quality rGO homogeneously dispersed within a silica-rich matrix was obtained.

2. Experimental procedure

All chemicals were obtained from Sigma–Aldrich and used as received. GO was synthesized using a modified Hummer's method based on reference [36]. Thus, 3 g of graphite were dispersed in a mixture of sulfuric (H_2SO_4) and phosphoric (H_3PO_4) acids (volume ratio of $\text{H}_2\text{SO}_4:\text{H}_3\text{PO}_4 = 8:1$). 18 g of potassium permanganate (KMnO_4) was subsequently added [37] and the mixture was refluxed at 60 °C for 12 h and poured over 400 ml ice mixed with 5 ml H_2O_2 (30%). The reaction mixture was centrifuged for 3 h at 6000 rpm in water, hydrochloric acid (HCl) (30%) and twice in ethanol. After each centrifugation step, only the finest solids were kept, whereas the coarse, non-exfoliated GO was removed. The obtained GO–ethanol dispersion was then dried at 40 °C under vacuum before re-dispersion in water.

The nanocomposites were prepared using different contents of GO, i.e., 0.1, 0.5, 1, 2, 3, 4, 5, 6, 10 and 20 wt% with respect to TMOS. The resulting samples are referred to as SG 0.1, SG0.5, SG1, SG2, SG3, SG4, SG5, SG6, SG10 and SG20, respectively. The GO–silica sols were prepared upon adding ethanol and TMOS to a dispersion of GO in water. The water content was adjusted to maintain a molar ratio of 1:1:0.1 between water, ethanol and TMOS [27]. The gelation process was performed at 60 °C and a pH value of 9 (controlled upon ammonia addition) [29,38]. The obtained wet gels were placed into a drying cabinet at 60 °C and allowed to age for 5 days. The resulting xerogels were first dried under vacuum, at room temperature, and then reacted for 24 h with hydrazine hydrate [18,13,39]. The subsequent pyrolysis processes were conducted at 900 °C under argon atmosphere. The pyrolyzed rGO–silica powders were pressed in graphite dies into monoliths (KCE hot press HP W 150/200, argon atmosphere, 30 MPa, 1600 °C, 30 min.). In order to avoid carbon diffusion into the samples from the graphite dies, their walls were covered with boron nitride.

FTIR spectroscopy was performed on a Bruker Vertex 70/70 v spectrometer for the prepared powders; whereas the monolithic samples were measured in Attenuated Total Reflection (ATR) mode with an Ivan 670 IR Spectrometer (Varian, USA).

Micro-Raman spectra were recorded using a Horiba HR800 micro-Raman spectrometer (Horiba Jobin Yvon, Bensheim, Germany) equipped with an Ar^+ (514.5 nm) laser. The excitation line has its own interference filter (to filter out the plasma emission) and a Raman notch filter (for laser light rejection). The measurements were performed with a grating of 600 g mm^{-1} and a confocal microscope (magnification 50 \times , NA 0.5) with a 100 μm aperture, giving a resolution of 2–4 μm . The laser power (ca. 20 mW) on the sample was attenuated in the range of 2 mW–20 μW using neutral density (ND) filters.

UV–vis spectrometry was performed on a Lambda900 spectrometer (PerkinElmer, USA). The band gap of the materials was estimated from the recorded UV–vis spectra using the Tauc relationship [40].

High resolution scanning electron microscopy was performed on a HRSEM, XL 30 FEG machine (Philips, Hamburg, Germany) equipped with Energy Dispersive X-ray Spectroscopy (EDX: EDAX Genesis, EDAX, USA). The high resolution transmission electron microscopy studies were done on a JEOL-2100F microscope (200 kV).

X-ray diffraction measurements were performed on a Bruker D8 Advance diffractometer (Bruker, USA) and on a Seifert PTS 3003 diffractometer for powders and monoliths, respectively.

Selected samples were analyzed additionally by means of atomic force microscopy (AFM, MFP 3D, Asylum Research, Oxford Instruments, USA) and conductive AFM (Orca) The electrical properties of the samples were assessed using four point resistance measurements (Keithley 2400 devices) and impedance spectroscopy (IS) was done with a Solartron SI 1287 Impedance Analyzer (Solartron Analytical, AMETEK, USA).

3. Results and discussion

3.1. GO synthesis and its conversion into rGO

Prior to the incorporation of GO into the silica sol, the quality of the prepared GO was assessed by means of Raman and FTIR spectroscopy. In Fig. 1(a), the Raman spectra of GO and the reduced material, rGO (obtained upon hydrazine exposition of GO followed by pyrolysis in argon) are shown. Due to the high degree of functionalization of GO, the single, well-defined 2D mode at 2704 cm^{-1} which is characteristic for graphene, is broad and of low intensity and it partially overlap with the D+D' and the 2D' bands to form a modulated bump from $2300\text{--}3400\text{ cm}^{-1}$, indicating either very small size of the graphene particles or a high density of defects [33,34]. Upon pyrolysis, the integrated intensity of the D band decreases with respect to the integrated intensity of the G band from 3.4 to 1.5. This reduction in the $I(\text{D})/I(\text{G})$ ratio is consistent with a less defective sample after pyrolysis. The FWHM of the D band decreases significantly after pyrolysis (almost by 50%), confirming that the defect density in the graphene sheets is reduced as a consequence of the removal of functional groups from GO during pyrolysis [21]. Additionally one can note that the 2D band does not shift upon pyrolysis. A shift of 2D is considered to rely on mechanical strain [41,42], which is consequently absent here. The G band shifts to lower wavenumbers (from 1602 cm^{-1} in GO to 1585 cm^{-1} in rGO). This is thought to rely on the reduction of GO (though the shift of the G band is less sensitive to intrinsic strain than the 2D band [21,41–47]).

The FTIR spectrum of GO (Fig. 1(b)) shows an absorption band at about 3400 cm^{-1} which was assigned to hydroxy groups

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