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The formation of silica nanoparticles on the polyacrylonitrile-based carbon nanofibers by graphene via electrospinning

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ABSTRACT

Silica/carbon nanofiber (CNF) composites have been successfully prepared by a graphene /polyacrylonitrile (PAN) solution containing tetraethoxysilane (TEOS) using electrospinning, followed by stabilization and carbonization. The graphene directly accelerates the formation and growth of nanosized silica particles on the fiber surface. The silica/CNF composites are characterized by SEM, TGA, FTIR spectra, a ^{29}Si MAS-NMR spectrum, and the crystallite parameters. This technology can be applied to prepare homogeneously dispersed nanosized metal-oxide particles on CNF composites.

1. Introduction

Recently, hybrid materials based on CNFs and silica nanoparticles have attracted significant scientific interest because of their remarkable properties, which cannot be obtained from the individual components [1,2]. Many research groups have been working on fabricating silica/CNF composites, which combine the advantages of both CNFs (nanoscale size, high specific surface area, and electrical conductivity) and silica nanoparticles (high strength, excellent heat stability, and good oxidation resistance) [3,4]. Nanoparticles formed on carbon materials are an important potential application for catalysis and the introduction of unique functions on the CNF surface because controlled nucleation and growth affords optimal chemical interactions and bonding, leading to very strong electrical and mechanical coupling within the hybrid [5,6]. Electrospinning is a unique method for producing the organic/inorganic hybrid composite nanofibers that uses a high voltage and a composite solution consisting of a metal precursor and a polymer solution [7]. In this work, we describe directly grown silica nanoparticles on graphene/PAN-based CNF composites produced by electrospinning of graphene/PAN solution containing TEOS. The structures and physical properties of these silica nanoparticles loaded on CNF composites were analyzed. Here, graphene is used as an ideal substrate for growing and anchoring functional nanomaterials for electrochemical devices or catalysts.

2. Experimental

The graphene used in this study were the xGNP-C750 grade materials produced by XG Science, USA. The 3 wt.% graphene (3 wt.% relative to PAN and TEOS) was immersed in dimethylformamide (DMF) and sonicated in a bath-type sonicator. The PAN and TEOS with a respective weight ratio of 7/3 were dissolved in homogeneous graphene-dispersed DMF solution. This mixture was continuously stirred at 60 °C until a homogeneous solution formed, and it was then cooled down to room temperature. This solution was fed into a positively charged spinneret attached to an electrospinning apparatus. The nanofibers were stabilized in air and then carbonized at 800 and 1000 °C under an argon atmosphere. The carbonized fiber fabricated at 800 °C was further heat-treated at 1200 and 1500 °C under an argon atmosphere for pyrolytic polymer-to-ceramic conversion. The samples were identified as PTG-800, PTG-1000, PTG-1200, and PTG-1500 by the heat-treated temperatures. For the pristine samples, PT-1000 and PG-1000, without either graphene or TEOS, were prepared.

SEM images with EDX spectroscopy were obtained using a Hitachi S-4700. The transmission electron micrographs (TEM) and the selected area electron diffraction (SAED) micrographs were taken with a TECHNAI-F20 unit (KJ111, Phillips) operating at 200 kV. FTIR spectra were recorded using a Nicolet 200 in the range of 400–4000 cm^{-1}. Solid-state ^{29}Si CP/MAS NMR spectra were obtained at 59.6 MHz using a Varian UnityINOVA600. TGA was carried out using a Shimadzu TGA

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50. The samples were heated up to 700 °C at a rate of 10 °C/min in air. XRD patterns were recorded using CuKα radiation ($\lambda = 0.15418$ nm) on a D-Max-2400 diffractometer. Backscattering Raman measurements were carried out with a Renishaw in Via-Reflex at room temperature. The crystallite parameters (d_{002}, L_c, and R) of composites were evaluated from XRD and Raman spectra [8]. R is the ratio of the integrated intensity of the D peak to the G peak from the Raman spectra. From the position of the (002) peak (2θ) in the XRD spectra, the interplanar spacing $d(002)$ was determined using the Bragg equation:

$$d_{(002)} = \frac{\lambda}{2\sin\theta_{(002)}}$$

where λ is the wavelength of the X-rays (0.15418 nm) and θ is Braggs's angle. From the position and the full-width at half-maximum intensity of the (002) peak, an attempt was made to estimate the crystal size L_c using the Scherrer equation:

$$L = \frac{K\lambda}{\beta\cos\theta}$$

L_c values were calculated from the peak width at half-maximum intensity, β, of the (002) peak, where $K = 0.9$ for L_c.

3. Results and discussion

The elemental analysis of the graphene was summarized in Table S1. The elementary analysis of graphene was characterized as 88.68% carbon, 0.79% hydrogen, 1.11% nitrogen, and 7.65% oxygen. The graphene with functional group can be dispersed in organic solvent. The functional groups on graphene provide reactive and anchoring sites for the nucleation and growth of nanomaterials [5]. The morphology of graphene, thin-stacked flakes with a well-defined few-layer structure at the edge, can be clearly observed in Fig. 1(a). PT-1000 (Fig. 1(b)) not associated with graphene consists of relatively uniform and smooth fibers without particles, while the PTG composites have an irregular distribution of nanoparticles. The SEM images (Fig. 1(c–e)) show the presences of uniform nanoparticles on carbon fibers surface after 800 °C pyrolysis. They represent that the nanoparticles are spherical shape and uniformly dispersed on the surface of the CNF composites. With increasing the heat-treatment temperature, the size of particles become larger and average fiber diameter decreased. The EDX spectrum and the corresponding elemental mapping results for the surface of the PTG-800 provided information about the distribution of C, O, and Si atoms in the fiber (Fig. 1(f)). The TEM images corresponding SAED of PTG-1200 and PTG-1500 are shown in Fig. 1(g–h). The images indicate that nanoparticles with an average particle size of 10–30 nm are successfully grown on the surface of CNFs in accordance to the SEM results. The corresponding SAED patterns are shown in Fig. 1 (g–h) inset. The halo SAED pattern of PTG-1200 shows that the nanoparticles are in the amorphous states, while that of PTG-1500 indicates that the nanoparticles consists of β-SiC structure with [1 1 1] and [2 2 0] crystal planes [8,9]. This evidence mentioned above can infer that the SiC nanoparticles in our experiment were formed through the reaction at high temperature: $SiO_2 + 3\,C \rightarrow SiC + 2CO$ [10]. The graphene edge and defect sites in the PTG composite can act as nucleation sites for silica [5]. Therefore, we suppose that functional groups

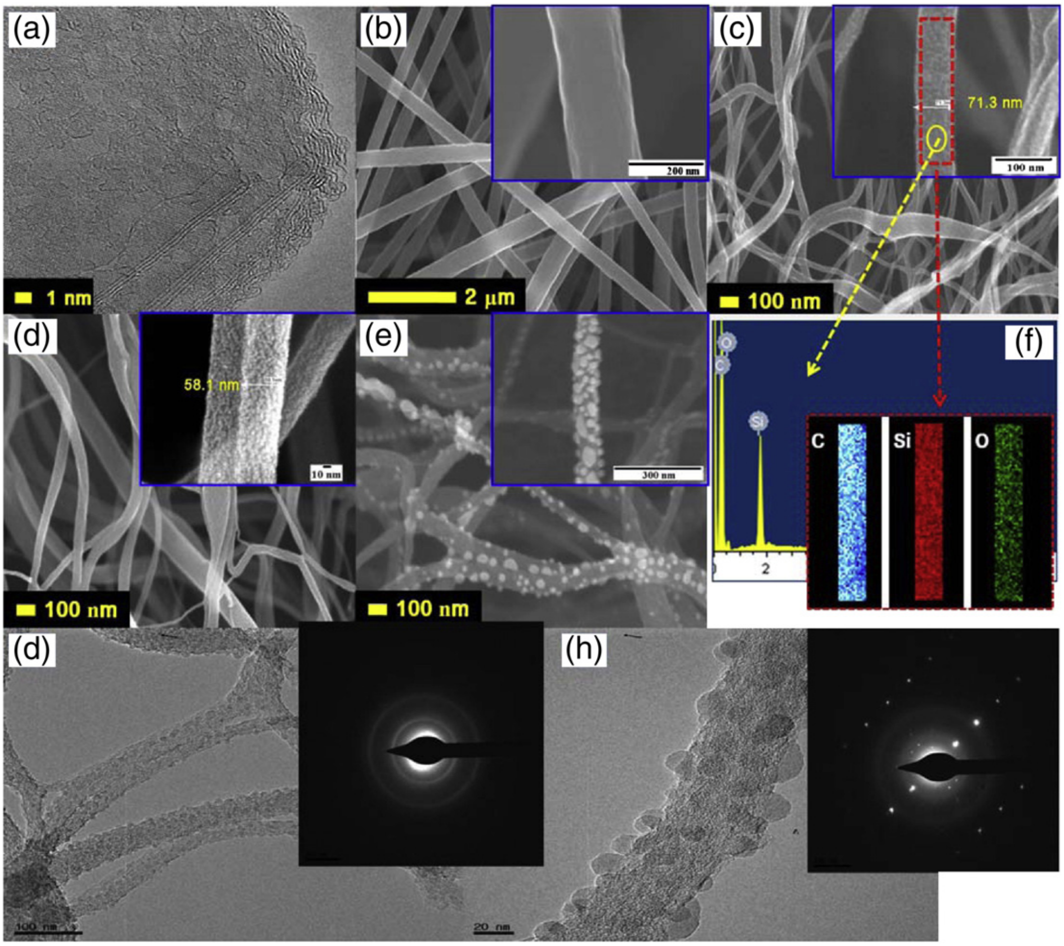

Fig. 1. (a) TEM image of OG. FE-SEM images showing (b) PT-1000, (c) PTG-800, (d) PTG-1000, and (e) PTG-1200. (f) EDX data and corresponding elemental mapping of an individual fiber; TEM images corresponding SAED of (g) PTG-1200, (h) PTG-1500.