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Grafting of carbon nanotubes onto carbon fiber surfaces by step-wise reduction of in-situ generated diazonium salts for enhancing carbon/epoxy interfaces

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ABSTRACT

Grafting of carbon nanotubes (CNTs) onto carbon fiber (CF) surfaces was achieved by a step-wise reduction of in situ generated diazonium salts in an aqueous solution. The CNT layers were regularly anchored onto the CF surfaces by using β-cyclodextrin molecular tubes for encapsulating the diazonium salts. The resulting CNT/CF hybrids allow for a significantly rougher surfaces, which should potentially improve the CF/epoxy interfacial shear strength through enhanced mechanical interlocking similar to Velcro hooks.

1. Introduction

Carbon nanotube (CNT)/carbon fiber (CF) hybrids have gained in particular attention for their high capacity in enhancing the CF/resin interfacial adhesion [1], because the CNTs can spread applied stress in different directions, which bind CFs and the resin together in a way similar to Velcro hooks [2]. There are three strategies for fabricating the CNT/CF hybrids. The most popular strategy is chemical vapor deposition (CVD) [3]; however, there is usually a significant degradation in tensile strength (TS) of CFs for high-temperature and metal catalysts [1]. An alternative method is electrophoretic deposition (EPD) [4]; but the physical interaction thus formed resulted in a poor stress transfer. Chemical grafting is recognized to be capable of significantly increasing the interfacial adhesion [5,6]. Nevertheless, the CFs have to be vigorously pre-oxidized to afford functionalities that often lead to damage of the CFs [7].

Since 1992, a mild and controllable grafting method for surface functionalization has been developed by reduction of aryl diazonium salts to covalently attach phenyl derivatives onto various surfaces, without damaging the substrates [8]. We present a novel method to prepare CNT/CF hybrids based on two-step diazoniunium reductions. The properties of CNT/CF hybrids and its composites were also characterized.

2. Experimental

The CFs were dipped into a HCl solution (0.5 mol L^{-1}) containing p-nitroaniline (4×10^{-3} mol L^{-1}) and β-cyclodextrin (4×10^{-3} mol L^{-1}). $NaNO_2$ (15 mg) was added to the reaction mixture and left for 5 h. The modified CFs were sequentially washed upon sonication in acetone, absolute alcohol and de-ionized water to remove the physisorbed species. Nitro groups on the CFs were then electrochemically reduced into amine groups in an electrochemical cell (CHI660E, China) equipped with the CF bundle as a working electrode, a Pt plate and a saturated calomel electrode as the counter and reference electrodes, respectively. We scanned the potential from −1.8 to −0.2 V at a rate of 0.1 V/s in a 10% ethanolic solution (KCl=1 mol/L) for five times to convert the nitro groups into amino groups. The amino-functionalized CFs were immersed in HCl solution (0.5 mol/L) containing 10 mg of $NaNO_2$ and 1.5 mg/mL of the acid-shortened MWCNTs to immobilize CNTs onto CFs. Thereafter, the CNT-modified CFs were washed upon sonication in acetone, alcohol and de-ionized water sequentially, and vacuum-dried for test.

The carbon nanotubes and carbon fibers were characterized by field emission scanning electron microscope (FE-SEM, JEOL, JSM-7001F, Japan) at an accelerating voltage of 10 kV. The samples were attached onto a copper stub with conductive adhesive for observation. The surface roughness of the carbon fibers was obtained by using an atomic force microscope (AFM, Nanoscope IV Digital Instruments, USA) in tapping mode. The sample for AFM was prepared by sticking carbon fiber filament on a cleaned glass

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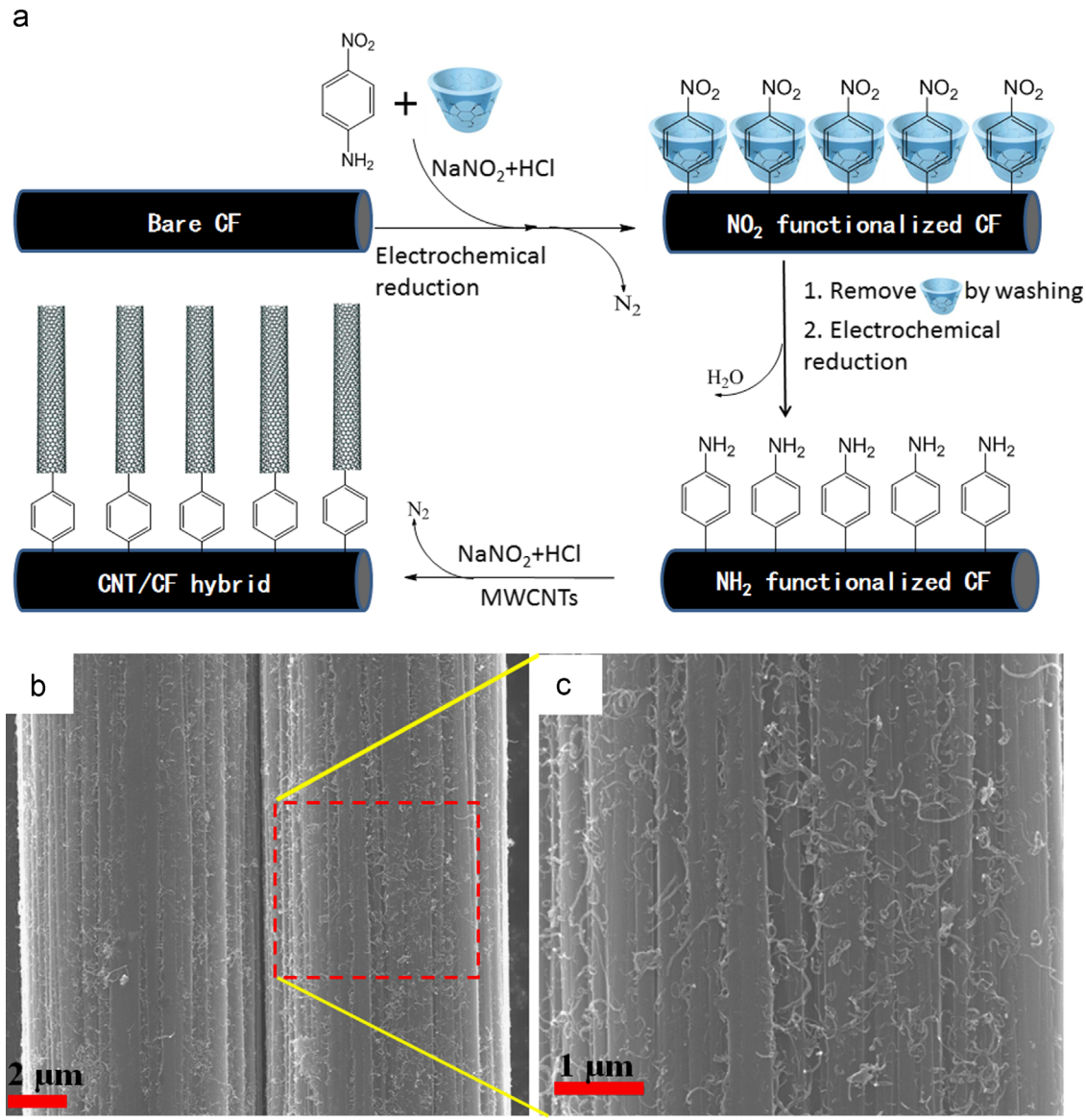

Fig. 1. (a) The schematic procedures involved in the grafting of MWCNTs onto CFs; (b) and (c) typical SEM images of surface morphologies for the CNT/CF hybrids.

substrate. An X-ray photoelectron spectroscopy (XPS) technique was used to analyze the surface chemistry of the fiber samples. The measurements were made on a Kratos XSAM800 spectrometer at a residual vacuum of 2×10^{-7} Pa, using a monocharomatic Al Kα Source (energy 1486.6 eV).

The CNT/CF hybrid fibers were cured by a mixture of E51 epoxy resin, triethylenetetramine and acetone with a weight ratio of 10:1:1. The curing conditions are: vacuum dried under ambient temperature for 20 min under a pressure of 0.08 MPa, then dried under ambient temperature and pressure for 12 h, curing at 80 °C for 1 h, and further curing at 120 °C for 1 h. After fully curing, the composites were tensile fractured at a rate of 1 mm/min, with a gauge length of 50 mm, and the fractured morphologies were observed by SEM.

The mechanical properties of the fibers were measured by a single fiber tensile tester (LLY-06E, China) with a gauge length of 25 mm and crosshead speed of 0.5 mm/min. A microbond test was carried out to determine the interfacial shear strength (IFSS) of the fiber/epoxy resin composites. A carbon fiber monofilament was fixed to a metal holder with an adhesive tape and be dropped with E51 epoxy resin to form microdroplets. The specimens were cured at 60 °C for 3 h. After curing, the microdroplets with the length of 40–80 μm were selected and examined by an interfacial strength evaluation instrument (Tohei Sayon Corporation, Japan) with a loading rate of 1 μm/s. The IFSS values were determined from Eq. (1). At least 40 measurements were tested for each fiber specimen.

Table 1
XPS surface compositions for the modified fibers.

Samples	C1s (at%)	O1s (at%)	N1s (at%)
Pristine CFs	88.03	11.06	0.91
NO_2-modified CFs	80.07	13.91	6.02
NH_2-modified CFs	82.55	12.47	5.98
CNT/CF hybrids	82.62	13.51	3.87

$$\tau_{IFSS} = F_{max}/\pi D_f L_e \quad (1)$$

where τ_{IFSS} is the interfacial shear strength, F_{max} is the maximum force, D_f is the diameter of the examined fiber, and L_e is the length of the fiber part embedded in the epoxy matrix.