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In situ study of copper electrodeposition on a single carbon fiber

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ABSTRACT

Copper metallization on carbon surface can improve physicochemical performances of carbon based materials and introduce multi-functionalities. This paper reports on the combined electrochemical characterization, *in situ* X-ray diffraction and fluorescence research, and scanning electron microscopic studies of nucleation and growth of Cu on individual carbon fibers. Compared to the flat glassy carbon substrates and Au thin film substrates, the onset potential of Cu electrodeposition on individual carbon microfiber is more negative with lower efficiencies, indicating the difficulty of Cu nucleation on carbon fiber surface. Utilizing the capability of synchrotron X-ray microbeam diffraction and fluorescence spectroscopy techniques, real time Cu crystalline structure and composition evolvement information during the electrochemical reaction processes have been studied. *In situ* study reveals random Cu grain formation and anisotropic growth. Dynamic Cu growth and dissolution were found to occur simultaneously during deposition. Cu nuclei density and size can be effectively controlled, in addition to the grain morphology and stability, indicating the possibility of electrochemical manipulation of microstructure thus the properties of Cu coated carbon materials.

1. Introduction

Polyacrylonitrile (PAN) based carbon microfibers, with their superior strength and modulus, high thermal and electrical conductivity, low thermal expansion coefficient and excellent chemical resistance, have seen increasing applications as the reinforcement component in composite materials to achieve higher performances [1–5]. Yet further improvement of the physicochemical properties of carbon fibers becomes challenging due to both the technical difficulties and cost effects. Because of the intrinsic inertness of carbon surfaces, wetting and bonding between the carbon fiber surfaces and foreign materials are often problematic [6]. Also the size and shape of the carbon fibers greatly affect the capability of conventional coating techniques, and effective deposition of well-controlled layers on a large number of carbon fibers is proved to be difficult. Tzeng and Chang [7] reported on using the electroless plating method to coat Ni and Cu on PAN-based carbon fibers based on a two-step approach, in which a sensitization and activation pretreatment step was first used to catalyzing the carbon fibers surface, and then followed by a acetone or high temperature treatment process to minimize the sizing effect. In these studies, copper and nickel deposition onto the carbon fiber has been demonstrated using the corresponding salt solutions and two powder-like displacing agents (Mg and Zn) at 90 °C. However, the results indicate that this multi-step electroless coating of carbon fiber surface lacks the deposit microstructure and uniformity control. Recently, we demonstrated that Ni layers can be effectively deposited on assembled interconnected carbon nanofibers (CNFs) to achieve significantly improved electric conductivity and better magnetic field alignment using electrochemical synthesis [8]. The electrochemical approach provides multiple adjustable experimental parameters and is capable of simultaneously coating of complex shaped surfaces. With additional advantages of low cost, high yield, low processing temperature and easy to scale-up, it shows great potential to become a powerful nanofabrication technique complementing the conventional physical and chemical synthesis methods.

Electrochemical deposition of Cu on foreign substrates has been extensively studied for over 50 years. Since early 1990s, damascene Cu electroplating on-chip metallization has been developed as a critical technology for microchip interconnection manufacturing [9]. Up to a 40–45% resistance drop in fully integrated devices using Cu interconnections compared to the Al(Cu) wiring has been demonstrated by D. Edelstein and coworkers [10]. For carbon fiber

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reinforced composites, Hage et al. found that the wettability of carbon fibers by the epoxy resin can be greatly improved by adding a electrodeposited copper interfacial layer [11]. In 2009, Li and coworkers [12] reported on using a three step electrodeposition-vacuum hot pressure-composite forming process to synthesize carbon fiber reinforced copper matrix composites. By adding an electrochemically deposited Fe layer, the interface bonding between Cu and C can be further strengthened. More recently, Li et al. [13] reported on the study of Cu electrodeposition on PAN based carbon fibers after surface treatment. It is found that the Cu deposition became more efficient after introducing surface functional groups. However, the experiments were performed on a bundle of carbon fibers under a single applied potential and quantitative characterization of the electrochemical processes is difficult to obtain.

In order to better understand metal nuclei formation and growth on carbon fiber surfaces, we have recently demonstrated X-ray *in situ* characterization approaches to obtain quantitative real-time structural and compositional information for Ni electrochemical processes [14]. In this paper, we report on the systematic study of morphology, microstructure and electrochemical behavior of Cu electrodeposition on single PAN based carbon microfiber. The use of *in situ* synchrotron X-ray diffraction and fluorescence spectroscopy analysis allows the simultaneous study of the deposited structure and composition during the electrochemical process. A dynamic Cu deposition and dissolution process has been identified through *in situ* study, which allows the control and optimizing of coating formation during electrodeposition.

2. Experiments

Carbon microfibers used in this study are high temperature graphitized polyacrylonitrile (PAN) fibers from Sigmatex with an average diameter of 6 μm. Before electrodeposition, all fibers were acid treated in diluted hydrochloric acid (12 wt.%) with ultrasonication for 30 min to remove residual surface amorphous layers and possible contaminations. No surface roughness change has been observed after the acid treatment.

Electrochemical experiments were carried out at room temperature (298 K) in ambient condition. A custom made three-electrode electrochemical cell was used for synchrotron experiments. Since

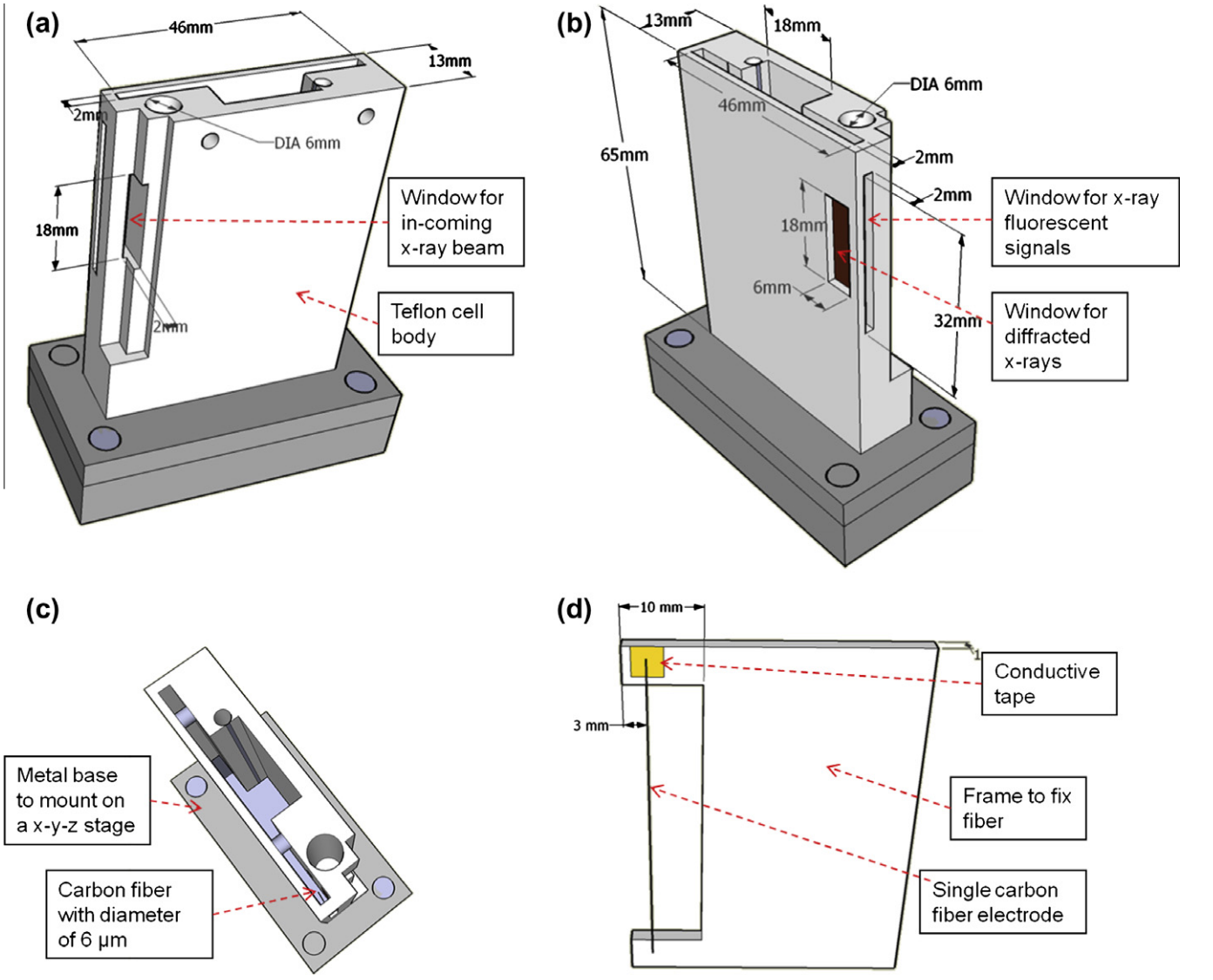

Fig. 1. Schematic drawings of the custom made three-electrode electrochemical cell from three different viewing angles (a–c) and a fiber frame (d). The dimensions of the cell have been indicated in (a) and (b), and fiber position has been indicated in (c).