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Letter to the Editor

## Polymer–metal complexes as a catalyst for the growth of carbon nanostructures

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### ABSTRACT

A universal technique is developed to coat uniform layer of catalyst on any targeted substrate. The technique is based on a novel concept of catalyst deposition by using polymer–metal complexes in the form of invertible polymeric nanostructures through molecular self-assembly. Growth of carbon nanofibres on carbon microfibrils was demonstrated to show this technique.

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Fibrillar carbon nanostructures (e.g. carbon nanotubes and nanofibres) with the diameter of 2–100 nm and length of 5–100 μm can be grown from catalytic decomposition of hydrocarbons on metal particles (e.g. iron, cobalt, nickel and their alloys) [1]. In the process, method of catalyst deposition, chemical properties of the substrate and interaction between the catalyst and the substrate are of the main factors which dominate the growth of carbon nanostructures and the properties of the resulting nanostructures [2]. The goal of catalyst deposition is to produce a uniform catalyst layer on the substrate, and therefore to guarantee an even coverage of the substrate with carbon nanostructures. To date, several methods have been developed to introduce the catalyst precursors onto substrate surface [3–6]. Among these, one particular application is to grow carbon nanofibres onto high-strength carbon microfibrils for the purpose of enhancing the debonding strength of these reinforcing microfibrils in advanced composites [3,6,7]. In all the techniques reported in the literature, the growth of carbon nanostructures on carbon microfibrils were fulfilled by means of careful manipulation and control of the process parameters including pre-treatment

of the catalyst species. In this Letter we propose a novel concept for deposition of metal salt precursor (in the form of polymer–metal complex) for the catalytic growth of carbon nanostructures onto the surface of reinforcing carbon microfibrils. For the first time, recently developed amphiphilic invertible polymers (AIPs) [8] have been applied for the catalyst deposition. The AIPs are based on poly(ethylene glycol) (PEG) (hydrophilic constituent) and aliphatic dicarboxylic acids (hydrophobic constituent) alternately linked in macromolecular chains. They form micellar nanostructures in solvents differing by polarity (Fig. 1). Variations of the polymer chain length and ratio of hydrophilic and hydrophobic units, molecular weight, and concentration result in the polymer self-assembly in selective solvents strongly differing by polarity [9]. Thus, in a nonpolar medium, the PEG constituents collapse and form the interior of the micelle, and the aliphatic dicarboxylic acid fragments switch their location to the outer side of the micelle.

The amphiphilic polymer used in the current study is polyester which is obtained by polycondensation of decanedioic (sebacic) acid and PEG-600 (S6) [8]. Based on the previous

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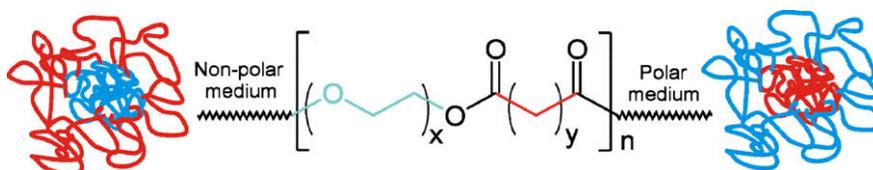


Fig. 1 – AIP molecular architecture in solvents strongly differing by polarity.

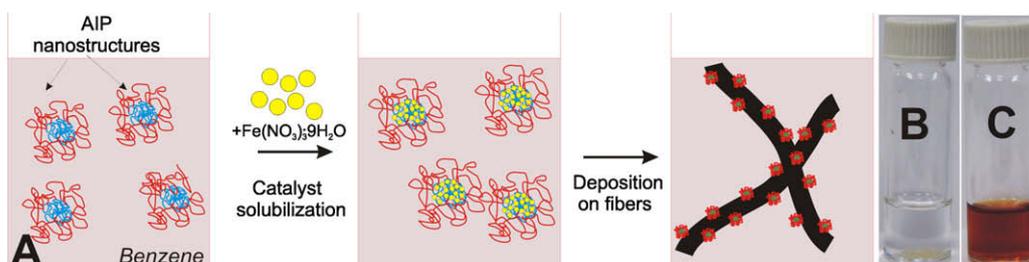


Fig. 2 – Scheme of the catalyst deposition on the surface of carbon microfibres (A). Physical appearance of ferric nitrate in benzene (B) and in AIP solution in benzene (C).

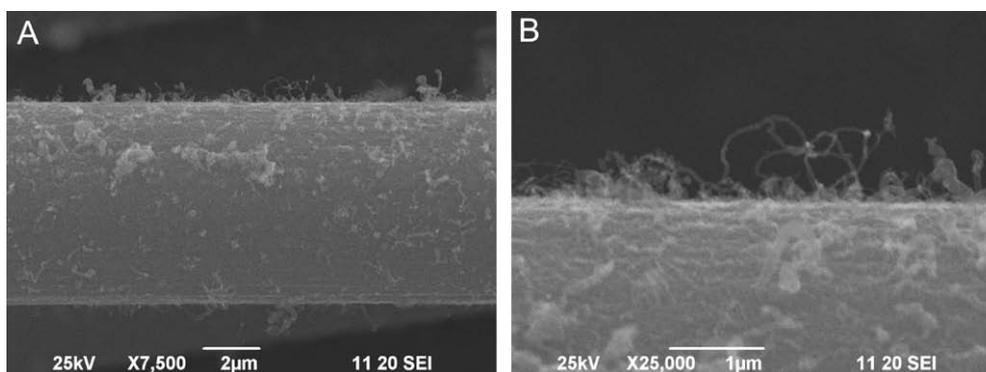


Fig. 3 – SEM images showing the catalytic growth of carbon nanostructures on the surface of carbon microfibres loaded with AIP–metal complex in benzene.

investigations [8,9], it is assumed that the catalyst precursor can be readily solubilized by PEG fragments of S6. Meanwhile, the hydrophobic polyester fragments with the high affinity to carbon will interact with the hydrophobic fibre surface and lead to uniform distribution of the catalyst onto the fibre surface. Moreover, it is expected that the size and concentration of the catalyst nanoparticles (developed by the conversion of deposited metal salt) on the fibre surface and, thus, the growth rate of carbon nanostructures can be controlled by the polymer concentration and solvent polarity.

To demonstrate this technique, sample of 24 K carbon fibre tow (Fibre Glax, OH) was cleaned in acetone (20 min) within a sealed bottle submerged in an ultrasonic tank (Branson ultrasonic cleaner B8510E-MT) before loading the metal precursors onto the fibre surface. To deposit the polymer–metal complex on the carbon microfibres, 50% (w/v) solution of amphiphilic invertible polymer S6 in benzene was first prepared (the solu-

tion had been stirred for 16 h at ambient temperature prior to further experimental steps). To prepare the polymer–metal complex, 70 mg of ferric nitrate  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$  (A.C.S. reagent, Aldrich) was added into 20 ml of the polymer solution. The mixture was gently stirred overnight to ensure solubilization of metal salt in the polymeric micelles. The formed light-brown transparent dispersion contained  $\sim 0.5$  mg/ml of  $\text{Fe}^{3+}$  ions. The scheme of catalyst deposition using the polymer–metal complex is shown in Fig. 2A. For comparison, the same amount of ferric nitrate was introduced into the benzene without addition of the polymer. The appearance of both the solutions is shown in Fig. 2B and C which indicates the successful solubilization of the metal salt by polymer fragments. When no polymer was added, the nonsoluble in benzene ferric nitrate is settled down. To deposit the polymer–metal complex, the microfibres were first immersed into the solution for 2 h, and then dried at  $120^\circ\text{C}$  for 10 h.

The growth of carbon nanostructures was performed by means of the thermal CVD technique in a tubular quartz furnace of 25 mm in diameter (Atomate Corporation, CA). The catalytic systems were reacted in C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> mixture (1:1) at 750 °C for 30 min. Mixture of H<sub>2</sub>/Ar (10% of H<sub>2</sub>) was used as the carrier gas (in a ratio 10:1 to the hydrocarbon gas mixture). After thermal CVD, typical carbon microfibre segments were selected for surface characterization. The characterization was performed using a scanning electron microscope (SEM) (JEOL JSM-6490LV) at an operating voltage of 25 kV. Fig. 3A and B shows the SEM micrographs of carbon microfibrils loaded with the polymer–metal complex after thermal CVD. It can be observed that the surface of the carbon microfibrils has been well covered with fibrillar carbon nanostructures. The presented concept can be considered as a universal way to coat any type of catalyst on a targeted substrate for the growth of carbon nanostructures. Besides, it can be applicable for broader range of substrates with complex morphology and micro-features.

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## Gadolinium and europium catalyzed growth of single-walled carbon nanotubes

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### ABSTRACT

The inner transition metals, gadolinium (Gd) and europium (Eu) have been shown to catalyze the growth of single-walled carbon nanotubes (SWCNTs) using chemical vapor deposition. The Gd and Eu nanocatalysts, prepared using a diblock copolymer templating method and characterized by atomic force microscopy, were uniformly spaced over a large deposition area with an average diameter of 1.9 nm and narrow size distribution. Characterization by transmission electron microscopy and Raman spectroscopy confirms the presence of SWCNTs catalyzed by Gd and Eu with an average diameter of 2.05 nm.

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Single-walled carbon nanotubes (SWCNTs) possess a number of interesting and unique physio-chemical properties suitable for a wide range of applications in material and biomedical sciences [1]. Understanding the synthesis/growth of SWCNTs is key to their technological development and remains a significant scientific challenge [2]. There are various

techniques used for the growth of SWCNTs including arc discharge, laser ablation, and chemical vapor deposition (CVD) [3]. Among these techniques, CVD is the most powerful and versatile method allowing large scale synthesis of high quality SWCNTs. This process utilizes metal nanoparticles as catalysts to allow carbon feedstock cracking, nucleation, and

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