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Controllable fabrication of carbon nanotubes on catalysts derived from PS-*b*-P2VP block copolymer template and in situ synthesis of carbon nanotubes/Au nanoparticles composite materials

Peng Xu¹, Xin Ji¹, Hongmin Yang², Junlei Qi², Weitao Zheng², Volker Abetz³, Shimei Jiang^{*1}, and Jiacong Shen¹

¹State Key Laboratory of Supramolecular Structure and Materials, Jilin University, 2699 Qianjin Avenue, Changchun 130012, P. R. China

²Department of Materials Science, Department of Chemistry and Key Laboratory of Automobile Materials of MOE, Jilin University, Changchun 130012, China

³Institute of Polymer Research, GKSS Research Centre Geesthacht GmbH, 21502 Geesthacht, Germany

E-mail: smjiang@jlu.edu.cn

Tel: 86 431-85168474

Fax: 86 431-85193421

Abstract

Highly ordered iron oxide nanoparticles with controlled size and spacing over a large surface area were prepared with polystyrene-*block*-poly(2-vinyl pyridine) (PS-*b*-P2VP) diblock copolymer template, the obtained nanoparticles could be used as catalysts for CNTs growth in a plasma-enhanced chemical vapor deposition (PECVD) system. This route offers the capability of controlling the density of CNTs on the substrate by altering the growing time, and aligned CNTs grew vertically onto the substrates with a pre-coating of aluminum oxide (Al₂O₃) layer. In addition, Au nanoparticles were successfully attached to the sidewall of deposited CNTs through in situ synthetic method.

1. Introduction

Carbon nanotubes (CNTs) have been demonstrated to possess unique electronic properties, excellent chemical and thermal stabilities, and a large surface area [1-3]. As a result, many researches have been devoted to develop devices that utilize these novel attributes, such as exploiting CNTs as transistors [4, 5], and as scan tips for atomic force microscopy [6]. At the same time, the synthesis of CNTs has widely developed. Chemical vapor deposition (CVD) is the most widely used method for its easy of operation and the CNTs are grown selectively on catalytic sites. Therefore, the diameter, location, and density of CNTs are thus largely dependent on the size, placement, and interparticle distance of catalyst nanoparticles [7, 8]. In the traditional CVD method, a metal thin film is first deposited on a surface using magnetron sputtering, then at high temperature, the film breaks apart and forms the metal particles as the catalyst for CNTs growth [9, 10]. So it faces the challenge of controlling the uniformity of catalyst size and growth intensity. Recently, many research groups have exploited effective methods to achieve controllable synthesis of CNTs. Template method is a fashionable method which is capable of rationally controlling size, spacing, and location of catalytically active nanoparticles. Except pores of alumina template membrane or ordered mesoporous silica templates [11-13], “soft template” derived from self-assembly of block copolymer has been demonstrated as a powerful method to generate well-ordered structures on the nanometer scale. Liu and co-workers reported the preparation of discrete Fe_2O_3

nanoclusters with uniform diameters on substrates from inversed micelles formed by polystyrene-*block*-poly(2-vinyl pyridine) in toluene loaded with FeCl₃, and these nanoclusters could be used as catalysts for growing single-walled carbon nanotubes by chemical vapor deposition [14]. In addition, polystyrene-*block*-poly(acrylic acid) and polystyrene-*block*-poly(4-vinyl pyridine) were also reported as templates for the synthesis of catalysts for CNTs growth [15, 16].

On the other hand, the unique properties make carbon nanotubes very useful for supporting nanoparticles in many potential applications, ranging from heterogeneous catalysis to molecular sensing applications [17, 18]. The formation of carbon nanotubes-metal nanoparticles composites has received increasing interest and various strategies have been adopted to attach metal nanoparticles on the surface of carbon nanotubes. Chemical functionalization of CNTs surface followed by the assembly of nanoparticles onto the CNTs via covalent, noncovalent, or electrostatic interactions are the most utilized methods defined as wet-chemistry strategies [19-23].

In this paper, uniformly sized iron oxide nanoparticles derived from PS-*b*-P2VP block copolymer template for the controllable synthesis of CNTs in a plasma-enhanced chemical vapor deposition (PECVD) system is reported. These substrates supported CNTs were directly aminatized by dipping the samples into an *N,N*-dimethylformamide (DMF) solution of polyethylenimine (PEI). Au nanoparticles on functionalized CNTs were obtained through in situ reduction of HAuCl₄ without the aid of reducing agents.

2. Experimental

2.1. FeCl₃-loaded PS-*b*-P2VP micelles

Polystyrene-*block*-poly-(2-vinylpyridine) (PS-*b*-P2VP) diblock copolymer was synthesized by sequential anionic polymerization of the different monomers ($M_n^{\text{PS}} = 34.2$ kg/mol, $M_n^{\text{P2VP}} = 41.8$ kg/mol, polydispersity index = 1.06) [24]. To obtain micellar solution, PS-*b*-P2VP was dissolved in toluene to yield a 0.25 wt % solution, FeCl₃ was then added to the toluene solution of PS-*b*-P2VP micelles (molar ratio of Fe³⁺/vinyl pyridine = 0.5) and stirred for at least 24 h.

2.2. CNTs obtained by PECVD

Thin films of FeCl₃-loaded micellar solution were spin-coated onto Si substrates or Al₂O₃-coated Si substrates at 2000 rpm, deposited iron oxide nanoparticles were formed by heating the sample in oven and were then used as catalytic substrates for the synthesis of CNTs in a PECVD system [25]. The PECVD chamber was pumped down to 20 Pa by a rotary pump, and then pure hydrogen (99.99%) with a constant flow of 20 sccm was maintained at 200 Pa. The thin film-coated substrate was heated to 800 °C in 40 min so that the iron oxide nanoparticles were reduced to zero valent metallic state. After that, pure methane (99.99 %) was introduced into the chamber for the growth of CNTs. During the growth process, a radio frequency power of 200 W (*I*

= 255 mA, $U = 900$ V) was applied and the substrate temperature was kept at 800 °C.

After certain time deposition, CH₄ inlet was shut off and the system was allowed to cool down to room temperature in H₂ atmosphere. Black thin films of carbon nanoparticles were obvious on the substrates.

2.3. CNTs/Au nanoparticles composite

The amination of the deposited CNTs was similar to that pioneered by Batteas's group [23], CNTs were grafted with PEI readily by protonation, and the amine groups behave like the amines of PEI in amidation chemistry, and the mainly deviation is dipping the Si wafer sustained samples directly to the PEI solution of *N*, *N*-dimethylformamide (DMF), the solution was kept at 50 °C and the sample was cleaned with acid before amination. Then the modified samples were dipped into the aqueous solution of H₂AuCl₄ (5 mM) at 60 °C for 30 min, after washing for 3 times, the samples were dried for examination.

2.4. Measurements

Scanning electron microscopy was done on a JEOL JSM 6700F field emission scanning electron microscope (FESEM). TEM observations were conducted with a Hitachi-8100IV transmission electron microscope operating at an acceleration voltage of 200 kV. TEM samples were prepared indirectly by depositing the solution onto

TEM grids which had been coated with carbon.

3. Results and discussion

For PS-*b*-P2VP diblock copolymer, toluene has preferential affinity to PS blocks, spherical micelles with a PS corona and P2VP core were formed at this concentration [26]. A variety of metal salts can be selectively coordinated to the PVP blocks [27, 28], here we added FeCl₃ to the micellar solution for fabricating iron oxide nanoparticles, which can be used as an effective catalyst for CNTs growth. Fig. 1a is a SEM image of the thin film of PS-*b*-P2VP micelles with iron ions which was fabricated by spin coating at 2000 rpm from the composite toluene solution on silicon wafers. The micellar film containing FeCl₃ was also investigated by TEM, since FeCl₃ gave obvious contrast in the images, we found FeCl₃ selectively formed in the P2VP domain that was the isolated core of the micelles (Fig. 1b). After heating the spin-coated micellar films in air at 500 °C for 2 h, the polymer was removed and iron oxide particles were left on the Si substrate [29-31]. Deposited particles are shown in Fig. 1c, and the diameter is about 40 nm.

The growth of CNTs on the fabricated catalysts was carried out in a PECVD system as described in the Experimental part. Fig. 2a-2c give the increasing density of CNTs on the substrates surface with increased CNTs growth time, which was qualitatively determined by translating over the substrate surface, about half of the catalysts on substrate can be seen in Fig. 2a (image of low CNTs of the 10 min

growth). Careful examination the images indicated that the average length of the obtained CNTs also increased as the growth time increased. It is reported that the Al₂O₃ thin layer promotes the formation of sufficiently small catalyst particles that are able to catalyze CNTs growth [32, 33], and the supporting layer for catalyst nanoparticles can significantly promote or hinder CNT growth by the nature of its physical, chemical, and electronic interactions with the catalyst [34]. As shown in Fig. 2d, it is worthy to note that higher yielded and better alignment of CNTs growing on the Al₂O₃ pre-coated Si substrate.

Polyethyleneimine (PEI), an amino-rich cationic polyelectrolyte, can be easily attached to the CNTs via physisorption on the CNTs sidewalls [35, 36]. It has been demonstrated that this way is an effectively approach to improve the solubility of the CNTs in solvent, and it can significantly change the electrical conductance of CNTs [37, 38]. But the direct attachment of PEI to the substrate sustained CNTs has been rarely reported.

The amination of the deposited CNTs has been given in the experimental part, the coated CNTs have a high density of imino- groups of surface, which can serve as primer for the adsorption of anionic AuCl₄⁻ followed by reduction of gold to zero state [39, 40]. By combination of the multifunctions of PEI, the attachment of gold nanoparticles on the sidewalls of CNTs is achieved. Fig. 3 represents the schmatic procedure of the preparation of CNTs/Au nanoparticles composites.

As shown in Fig. 4a, CNTs modified with Au nanoparticles were examined by SEM after heating, small dots appeared dense along the outerwall of CNTs in the

image. XPS was used to identify the chemical nature of the hybrid Au-CNTs. And the binding energy shown in Fig. 4b corresponds to the peak of Au 4f_{7/2} [41]. Fig. 4c shows the peak of C 1s core level with a binding energy of 285 eV [22].

The formation of gold nanoparticles attached CNTs is also confirmed by TEM images (Fig. 5), the samples were prepared by scraping from the Si substrate to TEM copper grid. Fig. 5a and 5b show the TEM images of CNTs before and after modification with gold particles. It can be seen that the gold nanoparticles preferentially adhere to the sidewall of CNTs with an average of 3-5 nm in diameter.

4. Conclusion

In summary, we demonstrated that a highly ordered iron oxide nanoparticles was effectively fabricated using thin film of diblock copolymer micelles in combination with thermal decomposition. The substrate sustained nanoparticles with controlled size and spacing over a large surface area are excellent catalysts for growing CNTs in a PECVD system, the density and length of these template synthesized CNTs obviously influenced by the growing times and the substrates nature. Aligned CNTs were easily formed onto the Al₂O₃ pre-coated substrate. Moreover, we successfully attached Au nanoparticles onto the surface of these substrate sustained CNTs with an in situ synthetic route. The method is expected to be more available and universal for preparing composites of CNTs and other noble metals.

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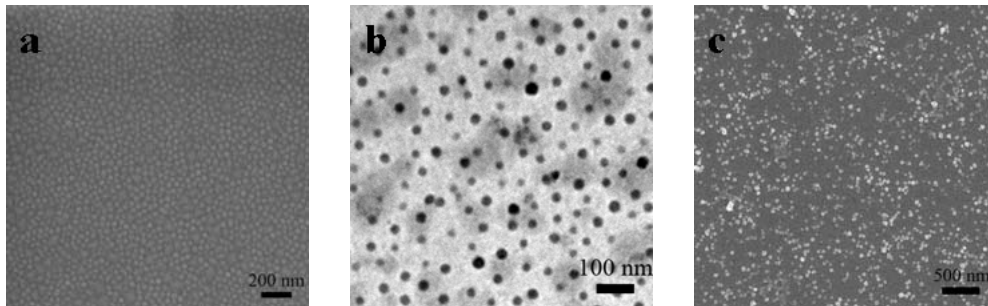


Fig. 1. SEM image of the micellar film from FeCl_3 -loaded PS-*b*-P2VP block copolymer (a); TEM image of the micelles formed by FeCl_3 -loaded PS-*b*-P2VP (b); SEM image of the resulting iron oxide nanoparticles (c).

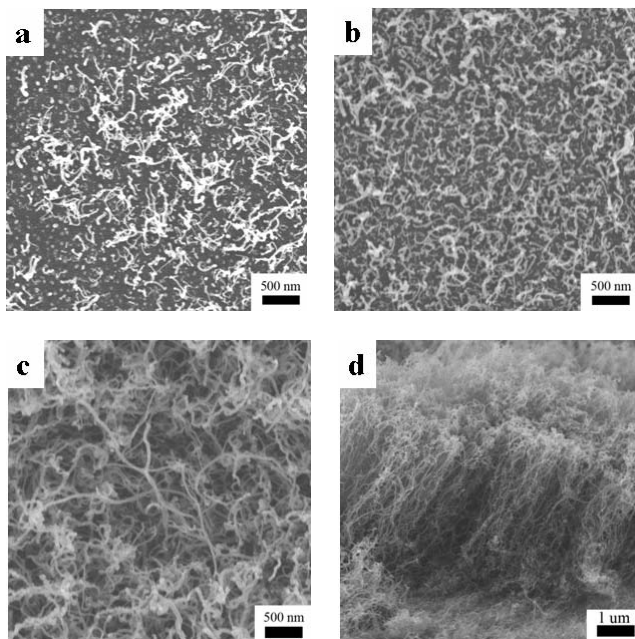


Fig. 2. SEM images of CNTs grown on iron oxide nanoparticles in a PECVD system for 10 min (a), 20 min (b), 30 min (c), 30 min with a thin Al_2O_3 film on Si substrate (d).

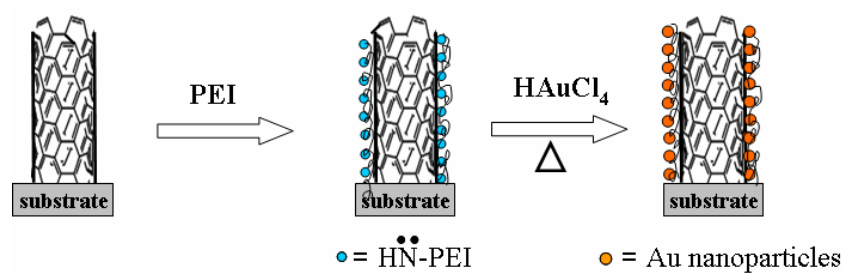


Fig. 3. Schematic illustration of the amination and the attachment of Au nanoparticles to the CNTs.

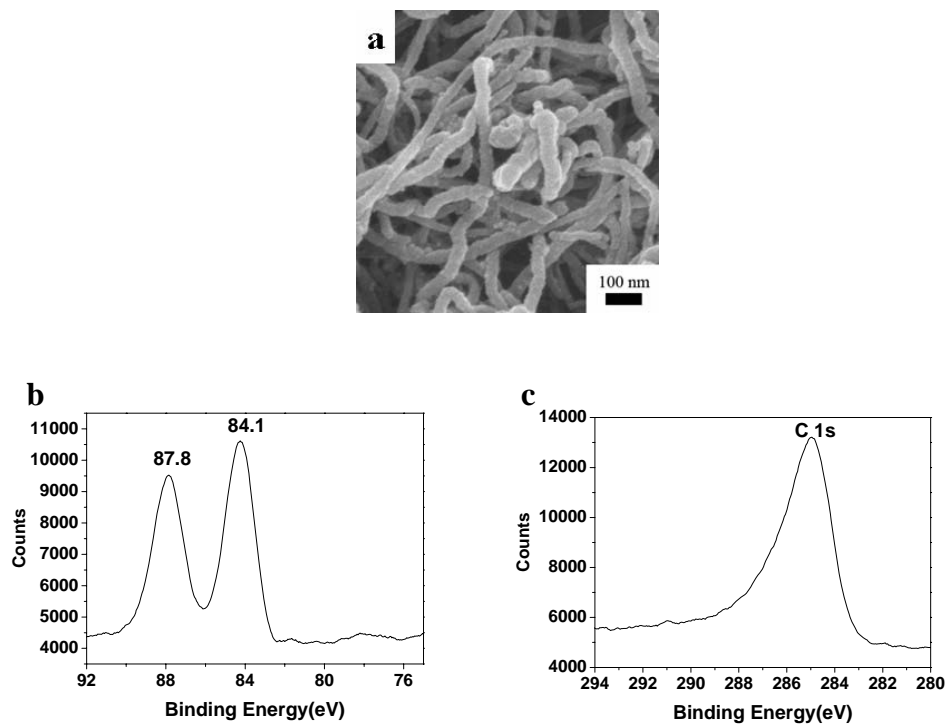


Fig. 4. SEM image of CNTs attached with Au nanoparticles on the surface (a), and the corresponding XPS spectra of Au nanoparticles (b) and C 1s core level (c).

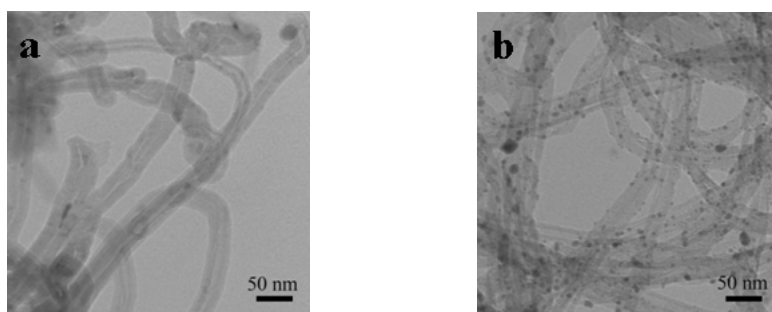


Fig. 5. TEM images of CNTs before (a) and after (b) the attachment of gold nanoparticles.