Reactive & Functional Polymers 69 (2009) 552–557

Contents lists available at ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Deposition of silver nanoparticles on single wall carbon nanotubes via a self assembled block copolymer micelles

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ARTICLE INFO

Article history:
Available online 20 January 2009

Keywords:
SWNTs
Block copolymer
Micelles
Ag nanoparticles
Thermal annealing
Nanocomposite

ABSTRACT

We demonstrate a facile route to decorate the surface of networked single walled carbon nanotubes (SWNTs) with silver nanoparticles (Ag NPs). The method is based on utilization of either spherical poly(styrene-*b*-4vinylpyridine) (PS-*b*-P4VP) or cylindrical poly(styrene-*b*-acrylic acid) (PS-*b*-PAA) copolymer micelles capable of stabilizing nanotubes in solution and subsequently forming a thin and uniform block copolymer/SWNTs composite film upon spin coating. The selective doping of silver acetate into either P4VP or PAA domains in a thin composite film, followed by thermal treatment, results in the formation of Ag NPs in the cores of micelles. Further heat treatment at 500 °C sufficiently high for degrading both block copolymers allows us to fabricate a thin SWNTs network in which Ag NPs are efficiently deposited on the surface of nanotubes. A sharp surface plasmon absorption band around 400 nm of the networked SWNTs with Ag NPs confirms the presence of Ag NPs with narrow distribution in their size.

1. Introduction

Single-wall carbon nanotubes (SWNTs)/metal nanoparticles (NPs) composites have recently emerged as new hybrid functional materials with properties useful for advanced application in catalysis, nanoelectronics, sensors and fuel cells [1–4]. The extraordinary chemical, mechanical and electronic properties of SWNTs [5–7] are efficiently combined with the unique physical and chemical properties of noble metal NPs [8], leading to unprecedented collective properties in the hybrid nanostructural materials [9–11]. For instance, the characteristic absorption band in UV-vis regime arising from surface plasmon resonance of metal NPs is potentially utilized for molecular waveguide and light harvesting purpose when coupled with that of SWNTs [12,13].

Hybrid type nanomaterials of SWNTs/metal NPs have been of great interest in the form of individual nanotubes or their bundles decorated with NPs [14–16]. There are many approaches for assembling metal NPs on the external wall of carbon nanotubes with various size, shape and distribution. The methods include *in situ* nanoparticle synthesis using chemical reduction of a metallic salt [17], electrochemical reduction [18], surface enhanced electrochemical reduction [19], alcohol catalytic chemical vapor deposition [20] and *ex situ* nanoparticle assembly method driven by electrostatic force and nanoparticle decoration onto chemically oxidized carbon nanotubes wall [21,22]. Further utilization of the metal NPs modified carbon nanotubes can be accomplished in the form of thin and networked films of the hybrid nanomaterial in particular based on the processes mostly applicable for industrialization such as spin and dip coating.

In most routes of synthesizing metal NPs with SWNTs in solution, the prime importance lies in the formation of a good carbon nanotube suspension in which individual nanotubes are separated with each other prior to the subsequent decoration with metal NPs. Poor dispersion of the SWNTs in most solvents results from stronger van der Waals attractions between nanotubes than the interaction between the solvent segment and the nanotube [23]. The destruction of van der Waals attraction becomes possible by an addition of a third element capable of preferentially interacting with the nanotubes, which therefore provides a space large enough to overcome a short range attraction between two nanotubes [23]. In addition, the requirement of the intrinsic opto-electric properties of SWNTs for collective coupling with metal NPs restricts the usage of "destructive" methods that significantly alter the surface of nanotubes via strong chemical reactions and thus modify the opto-electronic properties of nanotubes. In contrast the physical adsorption on the nanotube surface by low molecular surfactants and/or macromolecules such as synthetic polymers, proteins and DNA have been known "non-destructive" ways to stabilize SWNTs in both aqueous and organic medium [24–29].

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doi:10.1016/j.reactfunctpolym.2009.01.006

Furthermore, for thin uniform film formation of SWNTs by spin coating, a good SWNT suspension stabilized with *polymeric* dispersants is beneficial whose chain length is sufficiently long, ensuring homogeneous film formation during the process. When a polymer is used as the third element, unique long and flexible polymeric molecules wrap up the surface of nanotubes and prevent bare nanotube surface from exposing to the solvent media, which is reminiscent in many ways of colloidal particle stabilization in ternary systems [30]. By contrast, a suspension with small molecule surfactants usually results in serious re-aggregation of the nanotubes upon film formation. In particular, block copolymer dispersants have drawn great attention not only due to their excellent dispersion capability but also due to their intriguing capability to self assemble into unique self assembled nanostructures that can be utilized further in being incorporated with nanotubes [23,31,32].

Our recent work has also demonstrated a non-destructive method to fabricate transparent and low electric resistant nanocomposites of self assembled block copolymer (BCP) and SWNTs based on spin coating [33]. A good suspension of SWNTs was first obtained with BCP micelles in which the corona blocks physically absorbed onto surface of the SWNTs hindered the nanotube aggregation [31]. Site selective doping of metal salt facilitated the charge transfer to SWNT, leading to significant enhancement of electrical conductivity of a composite film. Self organizing BCP micelles capable of locating metal NPs selectively in their cores provides an interesting platform in which metal NPs can be easily incorporated on the surface of carbon nanotubes in thin films. In this contribution, we aim not only to decorate the surface of SWNTs with metal NPs templated with block copolymer micelles but also to fabricate thin networked film of the surface modified nanotubes on a substrate. Thermal annealing of a SWNTs/BCP micelle composite film spin coated with metal salt in their cores allows us to fabricate a thin SWNT networked structure in which the surface of the nanotubes is decorated with metal NPs.

2. Experiments

2.1. Materials

Poly(styrene-*block*-4vinyl pyridine) (PS-*b*-P4VP) copolymer (Mn, PS = 12,000 g/mol and Mn, P4VP = 11,800 g/mol, PDI = 1.14) and Poly(styrene-*block*-acrylic acid) (PS-*b*-PAA) copolymer (Mn, PS = 16,000 g/mol and Mn, P4VP = 4300 g/mol, PDI = 1.04), were purchased from Polymer Source Inc. Doval, Canada. Purified single walled carbon nanotube (SWNTs) prepared by using high pressure carbon monoxide method (HiPCO) at Rice University were used as received [34]. Silver acetate (AgAc) was purchased from Aldrich, Korea. Silicon wafer and glass substrates were cleaned using freshly prepared pirhana solution (70% H_2SO_4/30% H_2O_2) (Caution: pirhana reacts violently with organic compounds), rinsed with deionized water and dried in vacuum.

2.2. Deposition of Ag NPs on SWNTs

As shown in schematic diagram in Fig. 1, SWNTs were first dispersed in a diblock copolymer solution containing amphiphilic block copolymer micelles in toluene. 1 wt% PS-*b*-P4VP and PS-*b*-PAA solutions in toluene were prepared at 70 °C for 2 h and cooled to room temperature. A SWNTs stock solution was prepared in toluene by sonication. Small amount of SWNTs stock solution was added to the block copolymer solution and sonicated for 2 h with a power of 80 W, a frequency of 50/60 Hz for complete dispersion. The amount of SWNTs is 5 wt% with respect to block copolymer. Subsequently SWNTs/block copolymer solution was spin coated (SPIN 1200 Midas-system, Korea) on a cleaned Si wafer at 1000 rpm for 60 seconds and dried in vacuum at 50 °C for 1 day. 1 mmol aqueous AgAc solution (molar ratio of silver acetate/vinylpyridine ~ 1) was prepared at room temperature. A block copolymer/SWNTs composite thin film prepared on Si wafer was stained in AgAc solution and dried in vacuum desiccator. For thermal treatment, thin block copolymer/SWNTs films with AgAc salt were placed in heating stage (Linkem THMSE 600) and annealed at various temperatures for 2 hours.

2.3. Characterization

The morphology of the thermally annealed composite films was characterized by a Hitachi H-600 Transmission Electron Microscopy (TEM) operated at 50 kV, Atomic Force Microscope (AFM) (Nanoscope IV[a] Digital Instruments) in tapping mode and JEOL Scanning Electron Microscopy (SEM). TEM samples were prepared by carbon coating the thin block copolymer micelle film formed on either Mica sheet or Si substrate. Subsequently small sections of

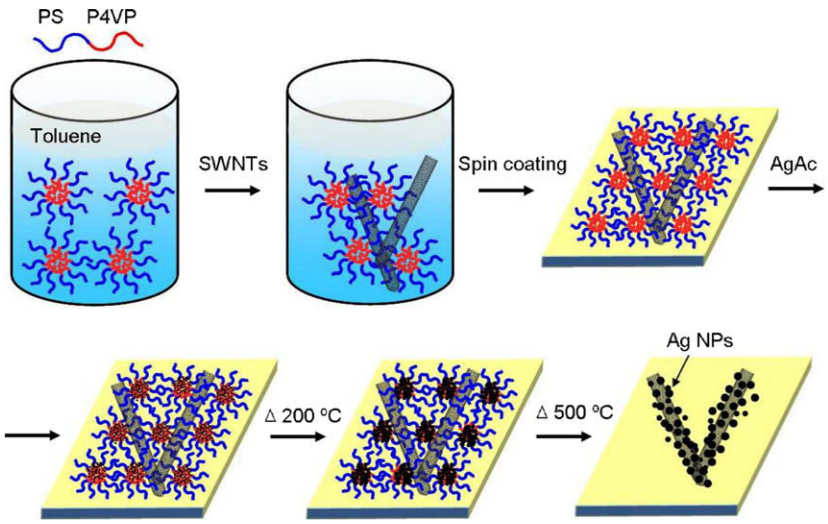

Fig. 1. A schematic illustration for fabricating thin SWNT network decorated with Ag NPs. Thermal annealing effectively converts AgAc selectively doped in the cores of spherical micelles into Ag NPs in a block copolymer/SWNTs composite film. Degradation of the block copolymer micelles at 500 °C leads to SWNTs network covered with Ag NPs on a substrate.