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Electro-conductive porous scaffold with single-walled carbon nanotubes in wormlike micellar networks

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ABSTRACT

A simple and rapid flow-induced microfluidic process is employed to disperse and encapsulate low volumes of single-walled carbon nanotubes (SWCNTs) in wormlike micellar networks, thereby forming an electro-conductive porous scaffold. SWCNTs with anionic surfactant sodium dodecyl sulfate (SDS) are first mixed with an aqueous wormlike micellar solution consisting of cationic surfactant cetyltrimethylammonium bromide (CTAB) and organic salt sodium salicylate (NaSal). The precursor mixture is then pumped through a microfluidic device containing hexagonal microposts at room temperature and ambient pressure, developing a soft scaffold with entangled bundle-like structures, containing interconnected SWCNTs and wormlike micelles. One-step microfluidic process presented in this work opens a new pathway to disperse and encapsulate SWCNTs in a micellar matrix without involving chemical reactions under ambient conditions, with promising potentials for sensing, encapsulation, and catalysis applications.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are cylindrical structures with diameters of 1–2 nm and lengths ranging from a few nanometers to tens of microns [1–4]. SWCNTs possess attractive properties (e.g., high electrical and thermal conductivity) for novel technological applications, such as in biosensors and field effect transistors [2,4]. The dispersion of SWCNTs in cationic, anionic and non-ionic surfactant solutions has been widely studied [5–11]. Surfactant molecules get absorbed onto the SWCNT surface to alter electrostatic interactions among SWCNTs, subsequently enhancing uniform dispersion of SWCNTs in solvents [12–16]. Factors such as the electric-charge, the size of the hydrophilic group, and concentration of the surfactant all affect the dispersion quality of SWCNTs. Anionic surfactant sodium dodecyl sulfate (SDS) has demonstrated promising results in dispersing SWCNTs in an aqueous environment, which de-bundles carbon nanotubes by electrostatic and steric repulsions [5,8,11–13,15]. Richard et al. [12] observed that SDS molecules were absorbed on the surface of SWCNTs, creating negatively distributed charges to prevent SWCNTs aggregations. They also reported that SDS molecules could be adsorbed perpendicular to the surface of SWCNTs, organizing into half-cylinders either along or perpendicular to the SWCNTs. Similarly, O'Connell et al. [13] reported that SDS molecules could bend and turn in radial position on the SWCNTs surface, forming concentric cylindrical structures. O'Connell et al. also showed that the

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orientation of SDS molecules promoted the formation of SWCNTs bundles. More recently, Calvaresi et al. [16] studied the effects of surfactant concentration on the self-assembly of surfactant molecules around SWCNTs by using dissipative particle dynamics simulations. Their simulation results showed that the mixture of SWCNTs and surfactant molecules could generate complex self-assembled morphologies.

In an aqueous pH buffer solution, the electronic properties of SWCNTs have displayed considerable changes due to the amount of hydroxide ions (OH^-) present in the solution, implying that SWCNTs can be potentially integrated into a pH sensor to detect chemical or environmental changes [17–24]. In fact, individual SWCNTs and SWCNT networks have been used to fabricate pH sensors [1–3,15,17,19–21,23]. SWCNT based pH sensors such as SWCNT-glass electrodes [19], polymer–SWCNT networks [20], and SWCNT nanobridges electrodes [21] showed increasing conductivity in the sensor as the pH value of the buffer solution increased. The complexity to isolate and interconnect individual SWCNTs in a device makes SWCNT network-based device more attractive. SWCNT networks possess large surface areas, are simple to fabricate, and readily scalable for industrial applications. For example, encapsulating SWCNTs in a scaffold carrier (e.g., polymers or gels) facilitates the formation of SWCNT networks for pH and other sensing applications [1,2,15,17,19–21,23]. However, most of the existing fabrication processes for SWCNT based pH sensors are tedious and costly, involve chemical procedures (i.e., chemical vapor deposition) and sophisticated equipment.

Motivated by this challenge, we propose a novel flow-induced microfluidic approach to synthesize electro-conductive SWCNT-based porous scaffold under proper hydrodynamic conditions by mixing dispersion of SWCNTs with a wormlike micellar solution. Synthesis of stable gel-like micellar structures from ionic wormlike micelles was first reported by Vasudevan et al. [25]. A semi-dilute ionic micellar precursor solution (CTAB with organic salt sodium salicylate (NaSal)) formed a gel-like *flow-induced structured phase* (FISP) after the wormlike micellar solution flowed through a microfluidic tapered channel packed with glass beads (20–100 μm in diameter). This irreversible gelation originates from a combination of the high rates of strain ($\dot{\epsilon} \sim 5000\ s^{-1}$) and from the extensional characteristics of the flow. Cardiel et al. [26] extended this study and reported the formation of FISP from both ionic shear thinning and shear thickening micellar solutions when subjected to strain rates $\sim 10^3\ s^{-1}$ and strains $\sim 10^3$. The FISP consists of entangled, branched, and multi-connected micellar bundles, evidenced by electron microscopy imaging. To our best knowledge, there is no reported research on the dispersion and encapsulation of SWCNTs in micellar gel-like structures for sensing applications.

In this work, we first prepared SWCNT dispersions in an aqueous solution with anionic surfactant sodium dodecyl sulfate (SDS). We then mixed the dispersion of SWCNTs with a semi-dilute ionic micellar solution containing cationic surfactant cetyltrimethylammonium bromide (CTAB) and organic salt sodium salicylate (NaSal) as the precursor solution. By pumping the precursor solution through a microfluidic device with microposts at room temperature and ambient pressure (see Fig. 1), SWCNTs were encapsulated in the gel-like FISP structure, yielding electro-conductive porous scaffolds consisting of bundled networks, assembled from SWCNTs and wormlike micelles. We also show proof of concept studies of using SWCNT-based electro-conductive scaffold for pH sensing.

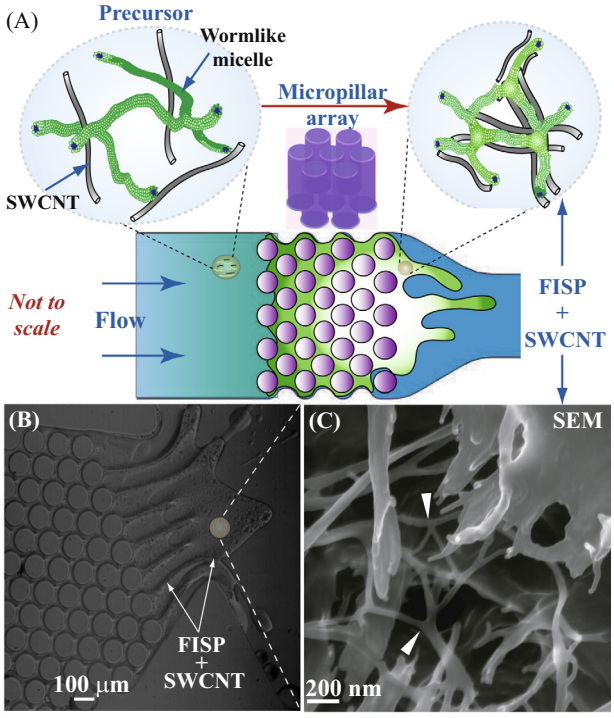

Fig. 1 – (A) Schematics of encapsulating SWCNTs in the gel-like flow-induced structured phase (FISP). When the IP–SWCNTs–SDS precursor was pumped through the microposts, highly entangled and multi-connected micellar networks encapsulated with SWCNTs were formed. (B) Optical microscopy image of the FISP–SWCNTs formed in the microfluidic device. (C) Scanning electron microscopy image (SEM) of the FISP with encapsulated SWCNTs. The white triangles highlight the branched structure made of SWCNTs and CTAB/NaSal wormlike micelles. (A colour version of this figure can be viewed online.)

2. Experimental methods

2.1. Dispersing single-walled carbon nanotubes (SWCNTs)

SWCNTs were purchased from Unidym-TM (HIPCO® Single-Wall Carbon Nanotubes) and used as received. Sodium dodecyl sulfate (SDS) was purchased from Sigma Aldrich and mixed with deionized water for the dispersion of SWCNTs. The utilization of surfactant-coated carbon nanotubes has become a standard procedure to uniformly disperse SWCNTs to enhance both materials and device performances [27,28]. We dispersed 1 wt% of SDS and 1 wt% of SWCNTs in DI-water and sonicated the mixture for 5 h. Note that the critical micellar concentration (CMC) of SDS in water is ~0.2 wt%. The dispersed solution was then incubated at room temperature for