Fabrication of carbon nano-tubes decorated with ultra fine superparamagnetic nano-particles under continuous flow conditions†

Suk Fun Chin, K. Swaminathan Iyer and Colin L. Raston*

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Ultra fine (2–3 nm) magnetite (Fe_3O_4) nano-particles are uniformly deposited on single-walled carbon nano-tubes (SWCNTs) pre-functionalised with carboxylic acid groups using microwave radiation. The deposition process involves chemical precipitation associated with continuous flow spinning disc processing (SDP), as a rapid, environmentally friendly approach which is readily scalable for large scale synthesis. The resulting decorated SWCNTs are superparamagnetic with specific saturated magnetization of 30 emu g^{-1}.

Introduction

Carbon nano-tubes (CNTs) receive much attention because of their outstanding electronic, mechanical, thermal, chemical properties and significant potential applications in nanoscience and nanotechnology.[1] Recently functionalizing CNTs with iron oxide superparamagnetic nano-particles (magnetite Fe_3O_4 and γ-Fe_2O_3 maghemite) have featured in many studies. This relates to their promising applications in the fields of fillers in polymeric materials, nanoprobes for magnetic force microscopy, wastewater treatment, biosensors, and drug delivery.[2–4] Various methods have been explored to attach iron oxide nano-particles to CNTs. In the case of Fe_3O_4 nano-particles, this includes the use of a carboxylic derivative of pyrene as an interlinker for the attachment of Fe_3O_4 nano-particles to the carbon nano-tube surface, and combining polymer wrapping and layer-by-layer (LbL) assembly techniques and the electrostatic attraction between templated amino-functionalized carbon nano-tubes and Fe_3O_4 nano-particles.[5–7] However, all these methods involve down-stream processing of purification/separation and the attachment of iron oxide nano-particles onto the carbon nano-tubes is poorly controlled. Therefore scaling up the synthesis of such composite material using this approach is difficult.

The alternative *in situ* synthetic approach is more promising and efficient in coating CNTs with magnetic nano-particles. This includes solvothermal and high temperature thermal decomposition of iron(III) acetylacetonate in the presence of multiwall carbon nano-tubes (MWCNTs) in polyol solution leading to the formation of Fe_3O_4 nano-particles attached to the carbon nano-tubes.[8,9] Even though Fe_3O_4 nano-particles have been reported to be uniformly attached to the CNTs surface with high coating density, the major drawbacks of this approach are that the reaction temperatures are very high, toxic/expensive organic solvents are used, high time/energy consumption, and scaling up may be problematic. Some effort has focused on the use of *in situ* chemical precipitation from solutions of $Fe^{2+/3+}$ using NH_4OH or NaOH to directly coat CNTs with Fe_3O_4 nano-particles, as a more environmentally benign, faster and more economic method. However, due to the lack of control of the synthetic conditions associated with typical bench-top batch chemistry, the size distribution of Fe_3O_4 nano-particles attached to the CNTs is very broad, ranging from 25–80 nm with low coating density. Moreover, the composite Fe_3O_4/CNT material is ferromagnetic rather than superparamagnetic.[10] The ability to control both the particle size and size distribution of Fe_3O_4 nano-particles and their loading behavior on CNTs is of primary importance for tailoring the physical and chemical properties of these materials,[11] yet it remains a synthetic challenge.

Spinning disc processing (SDP) involves a continuous flow reactor which has been recently shown to be effective in gaining access to a narrow size distribution of superparamagnetic Fe_3O_4 nano-particles in aqueous media using $Fe^{2+/3+}$ and base (see ESI).† The efficient SDP capability of fabricating metal (Ag, Au, Pt) plated CNTs also has been demonstrated with the metal uniformly layered around single wall carbon nano-tubes (SWCNTs) or metal nano-particles of narrow size distribution decorated on CNTs.[12,13] Thus SDP has potential for precisely controlling the size and size distribution of magnetic nano-particles attached to CNTs. In this paper we describe a novel yet simple method to coat superparamagnetic Fe_3O_4 nano-particles of narrow size distribution on SWCNTs *in situ* by modified chemical precipitation method using SDP in aqueous media at room temperature under continuous flow conditions.

Experimental

Spinning disc processor

SDP, Fig. 1, is a rapid flash nano-fabrication technique with all reagents being treated in the same way, and is in contrast to traditional batch technology where conditions can vary across the dimensions of the vessel.[14] The reagents are directed towards

Centre for Strategic Nano-Fabrication, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, 35 Stirling Highway, Crawley, WA, 6009, Australia. E-mail: clraston@cyllene.uwa.edu.au; Fax: +(618) 64881005; Tel: +(618) 64881572

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