Green synthesis of polymer monoliths incorporated with carbon nanotubes in room temperature ionic liquid and deep eutectic solvents

Li-Shun Zhang, Shu-Ping Gao, Yan-Ping Huang, Zhao-Sheng Liu*

Tianjin Key Laboratory on Technologies Enabling Development of Clinical Therapeutics and Diagnostics (Theranostics), School of Pharmacy, Tianjin Medical University, Tianjin 300070, China

ABSTRACT

In this work, an efficient method to prepare polymer monoliths with incorporated carbon nanotubes in a mixture of room temperature ionic liquid and deep eutectic solvents was developed. With assistance of the binary green solvent, 1-butyl-3-methylimidazolium tetrafluoroborate and choline chloride/ethylene glycol, single-walled carbon nanotubes were dispersed successfully in pre-polymerization mixture without need of oxidative cutting of carbon nanotubes, which may allow depletion of the emission of volatile organic compounds into environment. The novel single-walled carbon nanotubes monolith was evaluated by capillary electrochromatography. Compared with the monolith made without single-walled carbon nanotubes, the monolith with the incorporation of single-walled carbon nanotubes exhibited high column efficiency (251,000 plates/m) in the chromatographic separation. The morphology of the monolith can be tuned by the composition of mixture of ionic liquids and deep eutectic solvents to afford good column permeability and excellent separation ability for small molecules of alkyl phenones and alkyl benzenes. The results demonstrated that the method is a green strategy for the fabrication of multifunctional polymer monoliths.

© 2016 Published by Elsevier B.V.

1. Introduction

Multifunctional polymer nanocomposites that simultaneously possess high modulus and strength, high thermal stability, novel optical responses, and high electrical and thermal conductivity have been actively investigated [1,2]. Very gratifyingly, the appearance of composites of carbon nanotubes (CNTs)-polymer is developing new generation of ultrastrong lightweight materials since CNTs are ideal additives for the composites because of high flexibility, low mass density, and large aspect ratio (typically > 1000) [3,4]. For instance, their use as fillers in polymer-based nanocomposites offers tremendous potential for mechanical and transport property improvements even at low concentrations of CNTs. However, CNT aggregation has often been found when simply mixing CNT with polymers because van der Waals attraction between nanotubes is stronger than nanotube adhesion to polymers [5]. In this case, the key aspect is obtaining a uniform dispersion of CNTs within the polymer matrix, which is not always an easy task especially when the compatibility of CNTs with the polymer is poor.

A number of strategies have been developed so far to assist the dispersion of CNTs, including in situ polymerization [6–8], chemical surface modification of CNTs [9–11], and the third component assisted dispersion [12–14], among the most widely used. For example, the covalent modifications introduce various small organic groups onto the π-networks of CNTs to improve their solubility [6,7]. However, the disadvantage of this approach is that it may change the valuable electronic properties of CNTs and even introduce atomic defects and internal stresses into the nanotubes. Other inherently different processing routes have been attempted, and the tactics focus on addressing issues that affect composite properties, such as exfoliation of CNT bundles and ropes, homogeneous dispersion of the individual tubes into the matrix, alignment and interfacial bonding.

Over the last few years, as molten salts with a melting point below some arbitrary temperature, room temperature ionic liquids (RTILs) have emerged as excellent green reaction media for polymerization [15,16]. It has been found that RTILs could provide an effective and promising method to disperse CNTs [17,18], and even incorporate certain functionalities to improve their compatibility and stability since the hydrophobic interaction and the π-π stacking interaction are together involved between RTILs and CNT and increase the binding of RTILs molecules on CNT surface. Recently, deep eutectic solvents (DES) emerge as an alternative of

RTILs [19,20] formed by mixtures of hydrogen bond donors and halide salts (e.g., quaternary ammonium salts); they can be readily prepared and are relatively inexpensive with customizable compositions and properties compared with RTILs. The use of DES was also found to allow the dispersion of carbon nanotubes in the monomer solution [21].

One of the polymer nanocomposites for separation science is CNTs-entrapped porous monolithic columns. Monolithic columns are continuously attracting strong interest due to their unique characteristics such as high permeability and excellent mass transfer properties that arise from their flow through pores [22,23]. Recently, the incorporation of single-walled carbon nanotubes (SWCNTs) into the polymer monoliths has proven to be an efficient tool to increase the surface area of the polymer monolith and enhance the separation performance [24–27]. However, to avoid the sedimentation and aggregation of the pristine CNT, oxidative cutting of the pristine CNT is often preceded in a mixture of sulfuric and nitric acids before use, which may introduce atomic defects and internal stresses into the nanotubes.

In this study, we reported an efficient method of preparing CNT-incorporated polymer monoliths in a mixture of RTILs and DES. By our knowledge, papers concerning such multifunctional polymer nanocomposites prepared in RTILs and DES are not reported. In the appropriate proportion mixture of RTILs and DES, SWCNTs were found to be well-dispersed without need of oxidative cutting of SWCNTs and the resulting monolith with the incorporation of SWCNTs exhibited high column efficiency in the capillary electrochromatographic separation.

2. Experimental

2.1. Reagents and chemicals

3-(Trimethoxysilyl) propyl methacrylate (γ-MPS, 98%) was from Acros (Geel, Belgium). Butyl methacrylate (BMA, AR grade) and acetophenone (AR grade) were obtained from Bodi Chemical Reagent (Tianjin, China). Ethylene glycol dimethacrylate (EDMA, 98%) and 2-acrylamido-2-methyl-propanesulfonic acid (AMPS, 98%) were from Sigma-Aldrich (St. Louis, MO, USA). Azobisisobutyronitrile (AIBN, AR grade) was supplied by J&K CHEMICA Co. Ltd. (Beijing, China). Acetonitrile (ACN, HPLC grade) was purchased from Fisher (NJ, USA). 2,5-dihydroxyacetophenone (98%) was from Alfa Aesar (Tianjin, China). Butyrophenone (99%) was purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan). Choline chloride (ChCl, AR grade), ethylene glycol (EG, AR grade) and propylene glycol (PG, AR grade) were obtained from Kemiou Chemical Co. Ltd. (Tianjin, China). 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF$_4$, 98%), 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM]BF$_4$, 98%), 1-octyl-3-methylimidazolium tetrafluoroborate ([OMIM]BF$_4$, 98%) were purchased from Chengjie Chemical Co. Ltd. (Shanghai, China). Other analytical reagents were from Tianjin Chemical Reagent Co. Ltd. (Tianjin, China). Bare fused-silica capillaries with 100 μm ID and 375 μm OD were purchased from Xinnuo Optic Fiber Plant (Hebei, China). SWCNTs were obtained from XFNANO Reagent Co. Ltd. (Nanjing, China).

2.2. Preparation of SWCNTs monolithic capillary columns

A fused-silica capillary was rinsed with 1 mol/L NaOH followed by water for at least 30 min. Next, 0.4% (v/v) of γ-MPS solution in 0.006 mol/L acetic acid was pumped through the capillary for 1.5 h. The capillary was then flushed with acetone, dried in a steam of nitrogen, and left at room temperature overnight before use. DES was prepared by heating choline chloride and polyhydric alcohols mixture (molar ratio 1:2) to be molten in oil bath. SWCNTs

were sonicated in ionic liquid for 1 h using Sonics vibra cell model VCX 130. SWCNTs at a concentration of 10 mg/mL were used to as the pretreatment reagent. Further, other concentration of SWCNTs/[HMIM]BF$_4$ (5, 15 and 20 mg/mL) were also used as the porogens in the preparation of the monolithic stationary phases.

To prepare SWCNTs-incorporated monolith, the mixture of [HMIM]BF$_4$ and ChCl-PG was used as porogens, BMA as functional monomers, EDMA as cross-linking monomers, 1% (wt/wt%) AMPS as electroosmotic flow (EOF) provider and AIBN (1%, wt/wt%) as radical initiator (Table 1). After purged with nitrogen for 5 min, SWCNTs/[HMIM]BF$_4$ suspension were added in the pre-polymerization mixture and sonicated for another 15 min to suspend homogeneously and remove oxygen. The pre-polymerization mixture was introduced into the pre-treated capillary with a syringe. This suggests the surfactant-like properties of the mixture of DES and [HMIM]BF$_4$, enabling homogeneous dispersion of the SWCNTs in the pre-polymerization mixture (Fig. 1a). Following polymerization was conducted at 65 °C for 30 min, and the resulting monolithic column was rinsed with acetonitrile before the use for chromatographic analysis. To investigate the effect of SWCNTs on column permeability and retention properties, SWCNTs-free columns were prepared using the same polymerization mixtures. A detection window was fabricated at a distance of 9 cm from the outlet end of the monolith by burning out 2–3 mm segment of the polyimide outer coating. The corresponding reference capillary was prepared in the same way but without SWCNTs.

2.3. Capillary electrochromatography

Electrochromatographic experiments were carried out on a K1050 system (Kaiao, Beijing, China) equipped with a UV detector. A Lenovo personal computer with CXTH-3000 software for capillary electrophoresis was used. The total length of the capillary was 41 cm and effective length (polymer-based stationary phase) was 32 cm. The sample was introduced hydrodynamically for 3.0 s with 20 cm height difference between inlet and outlet. The electrolyte used was composed of ACN/acetate (pH 6.0) (10 mol/L ionic strength) (60/40, v/v). The entire buffer was made using ultrapure water and filtered with 0.2 μm membrane. The separation voltage was 15 kV. UV detection was performed at 254 nm. Column efficiency (N) was calculated by the following equation:

Table 1
Recipes of preparation for SWCNTs monoliths.

Columns	BMA	EDMA	[HMIM]BF$_4$ containing SWCNTs	[HMIM]BF$_4$	ChCl-PG
	(μL)	(μL)	(μL)	(μL)	(μL)
C1	7	3.6	9	32.4	48.6
C2	7	3.6	9[a]	32.4[a]	48.6
C3	7	3.6	9[b]	32.4[b]	48.6
C4	7	3.6	9	32.4	48.6[c]
C5	7	3.6	9	32.4	48.6
C6	7	3.6	9	40.5	40.5
C7	7	3.6	9	56.7	24.3
C8	7	3.6	9	64.8	16.2
C9	7	3.6	9[d]	32.4	48.6
C10	7	3.6	9[e]	32.4	48.6
C11	7	3.6	9[f]	32.4	48.6

[a] The amount of [BMIM]BF$_4$.
[b] The amount of [OMIM]BF$_4$.
[c] The amount of DES (choline chloride/ethylene glycol, 1/2, mol/mol).
[d] The concentration of SWCNTs in [HMIM]BF$_4$ was 5 mg/mL.
[e] The concentration of SWCNTs in [HMIM]BF$_4$ was 15 mg/mL.
[f] The concentration of SWCNTs in [HMIM]BF$_4$ was 20 mg/mL.