Available online at www.sciencedirect.com

ScienceDirect

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

Impact of surface modifications on hydrogen uptake by Fe@f-MWCNTs and Cu@f-MWCNTs at non-cryogenic temperatures

Madhavi Konni, Anima S. Dadhich, Saratchandra Babu Mukkamala *

Nanoscience & Nanotechnology Laboratory, Department of Chemistry, Institute of Science, GITAM University, Visakhapatnam 530045, A.P., India

ARTICLE INFO

Article history:
Received 30 June 2016
Received in revised form
11 September 2016
Accepted 13 September 2016
Available online xxx

Keywords:
Functionalization
p-MWCNTs
f-MWCNTs
Metal nanoparticles
Hydrogen uptake

ABSTRACT

A comprehensive study has been conducted to evaluate the hydrogen uptake capacity of carboxylate functionalized multi-walled carbon nanotubes (f-MWCNTs) after strategic incorporation of Fe and Cu nanoparticles on the surface. Metal decorated multi-walled carbon nanotubes (Fe@f-MWCNTs and Cu@f-MWCNTs) were prepared by refluxing various concentrations of metal precursor and f-MWCNTs in different reaction medium such as water, amine and DMF. The prepared materials were characterized by FT-IR, powder XRD, SEM, TEM and BET analyzer. The adsorption isotherms revealed that the hydrogen storage capacity of Fe@f-MWCNTs and Cu@f-MWCNTs was 0.55 and 0.68 wt%, respectively, at 253 K and 70 bar. Similarly, both compounds showed 0.39 and 0.5 wt% adsorption at 298 K and 70 bar, respectively. The uptake of hydrogen by metal decorated multi-walled carbon nanotubes was remarkably enhanced by a factor of 2 and 5 times that of Pristine MWCNT at 253 K and 298 K, respectively.

Introduction

Hydrogen is regarded as one of the most promising green energy carrier alternative to the existing fossil fuels for transport sector because of its high abundance, lightweight, and eco-friendliness [1,2]. One of the major obstacles for hydrogen technology is the lack of suitable adsorbing medium with high volumetric and gravimetric density for on-board applications [3]. Various materials, including the nanostructures and the bulk hydrides, have been examined in terms of their structures, energetics, and different properties for hydrogen storage applications [4–8]. The Department of Energy (DOE) has set the targets of volumetric (40 g/L) and gravimetric (5.5 wt%) hydrogen storage capacity by 2020 for on-board applications in automobile industry. But the fact that the reports on material confirming to the essential requirements of DOE are scarce, has led to elaborate investigations [9].

Carbonaceous materials such as carbon nanotubes (CNTs), graphene and fullerenes are some of the most promising physical adsorbents for storing hydrogen at non-cryogenic temperatures especially at room temperature [10]. Large surface area, superior chemical and physical properties like hollowness classifies the CNTs as elite entities for promoting hydrogen storage [11–13]. One of the drawbacks of bare CNTs is that the interaction with molecular hydrogen (H_2) is very weak and consequently the uptake of H_2 is not in the appreciable amount. In order to get the high volumetric and

* *Corresponding author.*
E-mail address: mscbabu@yahoo.com (S. Babu Mukkamala).

http://dx.doi.org/10.1016/j.ijhydene.2016.09.085
0360-3199/

gravimetric densities as well as improved binding of H_2 to CNTs, numerous studies have been conducted towards enhancement of porosity, surface area and number of defects by surface functionalization of CNTs [14,15]. One of the strategies for improving the hydrogen storage efficacy of CNTs is decoration with metal nanoparticles which strengthens the hydrogen–substrate interaction and facilitates the H_2 spill over to CNTs [16–18]. Many studies revealed that the hydrogen storage capacity could be significantly enhanced by incorporating different metals such as Pd, Co, Cu, Fe, and Ni on MWCNTs at ambient conditions [19]. Reyhani et al., reported enhancement of hydrogen storage capacity of Fe-MWCNTs to 0.75 wt% from Pristine's 0.3 wt% at ambient conditions by electrochemical hydrogen storage technique. Our earlier studies on Mg nanoparticle decorated MWCNTs had shown that experimental conditions such as solvent and metal concentration played an important role for improving the hydrogen uptake [20].

In the present study, the results of Fe and Cu nano particle decoration on f-MWCNTs under different experimental conditions such as variable metal concentrations and solvents (water, triethyl amine and dimethyl formamide), for improving hydrogen storage capacity of the material, have been discussed.

Experimental

Materials and synthesis

All chemicals were of analytical grade and used without any further purification. $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$ and triethyl amine were purchased from Merck. Dimethyl formamide (DMF) was purchased from Fisher Scientific.

Purification of MWCNTs
The raw MWCNTs were placed in a silica crucible and calcined in the furnace for 2 h at 500–520 °C followed by the treatment with 6.0 M HCl for 6 h at 95 °C. After heating, the MWCNTs were washed several times with deionized water until the pH of the solution was neutral. It was then dried overnight at 40 °C to get the Pristine MWCNT (p-MWCNT).

Functionalization of p-MWCNTs (f-MWCNTs)
The solid solution of 0.3 g of the p-MWCNTs and 150 ml of nitration mixture (1:3 HNO_3 and H_2SO_4) was refluxed for 48 h under magnetic stirring. The resulting solid was filtered and washed up to neutral pH. The sample was dried overnight in vacuum at 40 °C.

Decoration of Fe and Cu nanoparticles on f-MWCNTs
200 mg of carboxylate functionalized MWCNTs (f-MWCNTs) and 0.02 mol [8.08 g of $Fe(NO_3)_3$/4.83 g of $Cu(NO_3)_2$, High metal concentration (M^{HC})] or 0.01 mol [4.04 g of $Fe(NO_3)_3$/2.42 g of $Cu(NO_3)_2$, Low metal concentrations (M^{LC})] were taken in a 500 ml round bottomed flask. To this, 150 ml distilled water/150 ml distilled water containing 0.5 ml triethyl amine (TEA)/150 ml dimethyl formamide (DMF) was added and mixed thoroughly. It was then heated for 6 h at 80 °C (solution pH of aqueous medium was 6.8 and TEA medium was 10.2). The resulting solid was washed till the pH was neutral. The sample was dried overnight at 40 °C in vacuum.

Characterization

The morphology/texture of the obtained compounds (p-MWCNTs, f-MWCNT, Fe@f-MWCNTs and Cu@f-MWCNTs) was examined using FEI Quanta 200 FEG Scanning Electron Microscope (SEM) & Philips CM200 Transmission Electron Microscope (TEM). IR spectra were recorded on PerkinElmer "Spectrum two FT-IR" system using KBr pellet preparation method. Diffraction patterns were recorded by using PANalytical X'Pert PRO powder X-ray diffractometer with graphite monochromatic CuKα ($\lambda = 1.5406$ Å) radiation at room temperature.

Hydrogen storage capacity

The high pressure hydrogen adsorption measurements for the synthesized materials were conducted on BELSORP-HP (BEL, Japan). Initially the material was heated thoroughly at different temperatures under dynamic vacuum until the outgas rate was stable in the instrument. After activating the material for sufficient time, the weight of the sample was calculated again and the weight difference between the two could give an idea about the assessment of evacuation of solvent guest molecules from the pores. Then the material's hydrogen storage capacity was measured at different temperatures (253 K and 298 K) and pressures up to 70 bar. To get accurate results, ultra-pure (99.9999%) helium and hydrogen gases were used for the measurements.

Results and discussion

Morphology/texture

The TEM images of p-MWCNTs are shown in Fig. 1. Magnified TEM images of p-MWCNTs are shown in Fig. 1b and c. The average diameter of carbon nanotube is 30 nm. Usually, a significant decrease in tube length, change in texture, and/or an opened end-cap structure is observed in functionalized CNT synthesized by chemical oxidation methods. In our experiments, morphology/texture, length and diameter were well-retained in carboxylate functionalized MWNTs (Fig. 1d). Careful examination of TEM images revealed that both morphology/texture and end-cap structure of carbon nanotubes with the average diameter of CNTs about 30 nm was well-reserved in f-MWCNTs. For metal decoration of f-MWCNT to produce Fe-@f-MWCNTs and Cu@f-MWCNTs as well as to identify the optimum conditions for designing materials with efficient hydrogen sorption properties, a number of chemical reactions were conducted by changing the reacting media and the metal concentration. Figs. 2 and 3 depict the SEM and TEM images of Fe-@f-MWCNTs and Cu@f-MWCNTs. As shown in Figs. 2b and 3b, Fe and Cu was observed on the outer walls of the MWCNTs. EDAX analysis was also employed to determine the metal content in the synthesized sample. The present study results showed that the amount of Fe and Cu doped into the MWCNTs at M^{HC} in DMF medium was about 26.83 wt% and 53.95 wt%, respectively (Figs. 2d and 3d).

Please cite this article in press as: Konni M, et al., Impact of surface modifications on hydrogen uptake by Fe@f-MWCNTs and Cu@f-MWCNTs at non-cryogenic temperatures, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.09.085