



Morphology-controllable synthesis and characterization of carbon nanotube/polypyrrole composites and their hydrogen storage capacities



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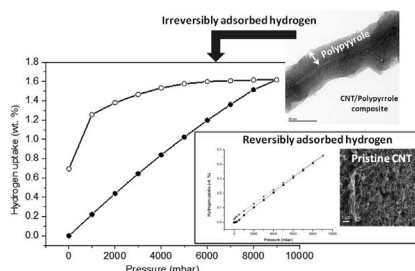
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HIGHLIGHTS

- Growth mechanisms of polypyrrole are controlled by changing monomer concentration.
- Lamellar structure is formed by using pristine CNT at high monomer concentration.
- Homogeneous polymer coating is achieved on the surface of oxidized CNT.
- CNT/polypyrrole composite has the highest hydrogen adsorption capacity (1.66 wt%).
- Polymer coating and chemical oxidation affects hydrogen sorption isotherms.

GRAPHICAL ABSTRACT



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ABSTRACT

Sphere-like and layer-by-layer growth mechanisms of polypyrrole are controlled by changing pyrrole monomer concentration and using carbon nanotubes (CNT) as template. Pristine polypyrrole has sphere-like structures but remarkable change in types of polypyrrole growth is observed from spherical-like to layer-by-layer structures in the presence of CNT. Acid treatment enhances polypyrrole coverage on CNT surface by preventing agglomeration of polypyrrole due to an increase in surface oxygen groups and sp^2 bonds in CNT structure. The crystallinity of powders comparably decreases after polypyrrole coating due to the amorphous structure of polypyrrole and a sharp decrease in the intensity of 002 peak. The influence of surface functionalization and polymer coating on the structural parameters of multi-walled CNT and their composites is investigated by tailoring the feeding ratio of polypyrrole. The hydrogen sorption measurements at ambient conditions by Intelligent Gravimetric Analyzer demonstrate that hydrogen uptake of CNT/polypyrrole composite is 1.66 wt.% which is almost 3 times higher than that of pristine CNT. Higher hydrogen uptake values are obtained by keeping the mass ratio of pyrrole monomer and CNT equal by using non-functionalized CNT in composite production. Hydrogen adsorption/desorption kinetics of polypyrrole/CNT composites is improved by increasing adsorption sites after

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polymer coating and acid treatment. The desorption curves of these modified surfaces are higher than their adsorption curves at lower pressures and hysteresis loop is observed in their isotherms since hydrogen is chemically bonded to the modified surfaces by the conversion of carbon atoms from sp^2 to sp^3 hybridization.

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1. Introduction

Nanostructured polypyrrole (PPy) and their composites have received attention due to their remarkable properties such as high electrical conductivity, excellent thermal stability, and relative easy synthesis routes [1,2]. PPy based composites have potential applications in advanced technologies including chemical sensors [3], energy storage [4], solar cells [5], supercapacitors [6], and actuators [7]. PPy is synthesized by electrochemical or chemical oxidative polymerization methods [8–10]. Although electrochemical polymerization provides high controlled morphology and direct deposition of PPy structures, chemical oxidative polymerization is suitable for mass production and direct application [11]. The morphology, structure and stability of PPy are influenced by oxidant type, polymerization medium, dopant, concentration ratio of monomers and oxidant, temperature and polymerization duration [12]. However, the main driving force behind the formation of laminar or spherical PPy structure in different reaction systems still is not clear. Liu et al. [13] demonstrated that granular structure of PPy is formed at initial stages of reaction whereas the structure is turned into short and straight fibers by increasing the reaction time. Especially the rate of oxidant addition affects on the formation of different types of PPy structures [14]. In addition, Han et al. [15] synthesized the hierarchical structure of PPy by adjusting the concentration of pyrrole and surfactant. He et al. [16] changed the morphology of the PPy from granules to short coral-like nanowires by decreasing pyrrole monomer and then produced three-dimensional nanowire networks by increasing the concentration of pyrrole monomer and mixing with poly(vinyl-alcohol) used as an additive. Therefore, the addition of polymeric materials during PPy polymerization brings a new insight to understand the changes in PPy morphology.

There are some reports on the use of conductive polymers as hydrogen storage media with acceptable hydrogen storage capacities. Pannelle et al. [17] found no hydrogen storage on HCl-treated polyaniline and PPy by volumetric measurements at room temperature and 77 K. On the other hand, the composites of PAni/CNT stored just under 0.5 wt.% hydrogen at 125 °C [18]. PPy/CNT composite is generally utilized as a supercapacitor material due to its high capacitance values [19]. Among recently developed hydrogen storage materials, CNT have attracted great attention due their structural and characteristic properties [20–23]. In the first work on hydrogen storage capacity in CNT reported by Dillion et al. [24], single walled CNT could store 10 wt.% of hydrogen at room temperature. In the literature, there is a big contradiction in hydrogen uptake of CNT at room temperature, and the values larger than 1 wt.% cause doubts since the results of the hydrogen uptake for the same material are not repetitive. To resolve this controversy, there have been a wide range of studies involving various carbon materials. Tibbetts et al. [25] showed that the largest hydrogen storage capacity of CNT at room temperature is less than 0.1 wt.% by comparing nine different carbon materials at the pressure of 11 MPa and temperature from –80 to +500 °C.

In the present study, conductive polymer is combined with the structural properties of CNT in order to increase the hydrogen

storage capacity of CNT for its utilization in energy storage devices [11,26]. At this point, PPy is chosen among various conducting polymers to produce CNT composites due to its relatively easy synthesis, high electrical conductivity, and environmental stability [27]. The PPy morphology and its growth behavior were investigated by changing the concentration of pyrrole monomer, and keeping monomer/oxidant ratio constant, and adding functionalized and non-functionalized multi-walled carbon nanotubes (MWCNT) in the reaction mixture. The surface of CNT was covered by PPy at different feeding ratios and structural changes were observed by several characterization techniques. The functionalization of CNT surface was achieved by acid treatment allowing proper dispersion and providing appropriate interfacial adhesion between CNT and PPy. Moreover, the effects of polymer coating and acid treatment on gravimetric hydrogen storage capacities of PPy/CNT composites were examined by Intelligent Gravimetric Analyzer at room temperature in the range of 1000–9000 mbar.

2. Experimental section

2.1. Materials

Multi-walled carbon nanotubes (MWCNT, Baytubes, purity >95%), pyrrole (Py, C_4H_5N , Merck, 98%), potassium dichromate ($K_2Cr_2O_7$, Chempur, 99.9%), ferric chloride ($FeCl_3$, Aldrich, 97%), sulfuric acid (H_2SO_4 , Fluka, 95–97%).

2.2. Chemical oxidation of CNT

Oxidation process was performed for the functionalization of MWCNT surface. MWCNT (5.0 g) were mixed into the mixture of potassium dichromate (10.5 g), sulfuric acid (150 mL) and 7.5 mL distilled water at 45 °C for 24 h [28]. In this process, the samples were filtered and washed with distilled water several times. All samples after filtration process were dried in a vacuum oven at 60 °C overnight.

2.3. Synthesis of CNT/PPy composites

PPy was coated on both MWCNT and oxidized MWCNT by *in situ* polymerization of pyrrole (Py) monomer by using $FeCl_3$ as an oxidant in ethanol:water (1:1, v/v) for 24 h through refluxing [27]. Fig. 1 shows the schematic representation of PPy synthesis. In this reaction, the Fe^{3+}/Py molar ratio was kept as 2.4 during polymerization [29]. MWCNT-based composites were synthesized at

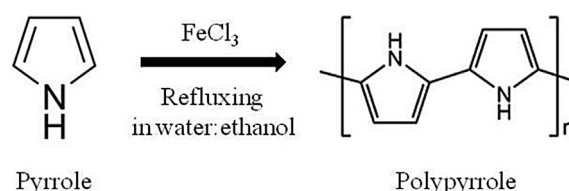


Fig. 1. Schematic representation of polypyrrole synthesis.

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