

Development of a novel material for hydrogen storage

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ABSTRACT

Nanocomposites of polymer and carbon nanotubes (CNTs) are fascinating and progressing area of hydrogen storage research. The dispersion of the CNTs in polymer matrices is an important issue while making the nanocomposites. In-situ polymerization is a better approach for synthesizing homogeneous polymer CNT composites. However, the dispersion of CNT in the monomer solution is still problematic. In this paper, we report a novel approach for dispersing multiwalled (MW) CNTs directly into polyaniline (PANI)/ethyl alcohol solution and preparation of uniform composite of PANI/MWCNT with the aid of nickel catalyst. The possibility of the preparation of uniform PANI/CNT suspension retaining the structure of both PANI and CNT is successfully demonstrated for the first time.

Key words: Carbon nanotubes, Polyaniline, Hydrogen storage, Composites

INTRODUCTION

A novel hydrogen storage medium is highly desirable for the next generation clean fuel. Metal hydrides are already showing good promise for future hydrogen storage. However, their relatively low gravimetry capacity is an obstacle for maximum hydrogen storage. Conducting polymers are safe, highly stable, light weight and economic materials. PANI is a unique type of conducting polymer in which the charge delocalization can, in principle, offer multiple active sites on the polymer backbone for the adsorption and desorption of hydrogen, involving weakening of the H-H bond followed by adsorption of this hydrogen onto the adjacent nano-fibrous network. However, the major disadvantage of polyaniline is its complicated processing due to its degradation below the melting point. In addition, major difficulties have been encountered in attempts to dissolve the material. The controversy on the solubility of polyaniline is dated back to 1910. Willstatter and Dorogi reported that an oligomeric (eight-monomer chain compound) aniline was largely insoluble [1]. Green et al repeated their experiments and claimed solubility of this non-polymeric material in 80% acetic acid, 60%

formic acid, pyridine and concentrated sulfuric acid [2]. Later, Angelopoulos and co-workers and Wang et al. reported only partial solubility of polyaniline, in its emeraldine base form, in N-methylpyrrolidone (NMP), dimethylformamide (DMF), tetrahydrofuran (THF), benzene and chloroform [3]. The strategies to render the conducting polymer solution processible, were progressed significantly in the following years also. A significant improvement in this field occurred when camphorsulfonic acid (CSA) [4], dodecylbenzenesulfonic acid [5] or alkylene phosphates [6] have been proposed as dopants. Composites of conjugated polymers are fascinating because of their potential for enhanced properties that are difficult to attain separately with individual components. It is reported that PANI can store as much as 6–8 wt% of hydrogen [7], however, the reproducibility is problematic due to the complicated processing [8]. In recent years many research work have been reported on PANI composites with CNTs [9]. The report demonstrates the compatibility between PANI and CNT. However, the exact nature of the composite still remains unclear and further study is required.

We report the synthesis of new PANI/CNT composite by the solubilization process using nickel catalyst. We recommend this material for hydrogen storage due to its combined properties. Fourier Transform Infrared (FTIR) analysis was done to study the nature of the material individually and in composite.

MATERIALS AND METHODS

The CNTs were purchased from Nanocyl, Belgium, and the purity of the sample is 95%. Polyaniline in emeraldine base form was purchased from sigma Aldrich. MWCNTs were functionalised using HNO₃/H₂O₂ medium and the PANI/MWCNT uniform solution (PANI/MWCNT/nickel composite) was prepared with the aid of nickel. The PANI/MWCNT/nickel composite was later filtered and dried at 60°C. Nickel used was in the form of powder. FTIR analysis was carried out using Nicolet NEXUS bench machine with 128 scans and resolution of 1 cm⁻¹. The IR samples were prepared by mixing the samples with KBr powder.

RESULTS AND DISCUSSION

FTIR spectra (400-4000 cm^{-1}) for CNT (a), PANI (b) PANI/CNT (c) and PANI/CNT doped with nickel (d) are shown in Figure 1.

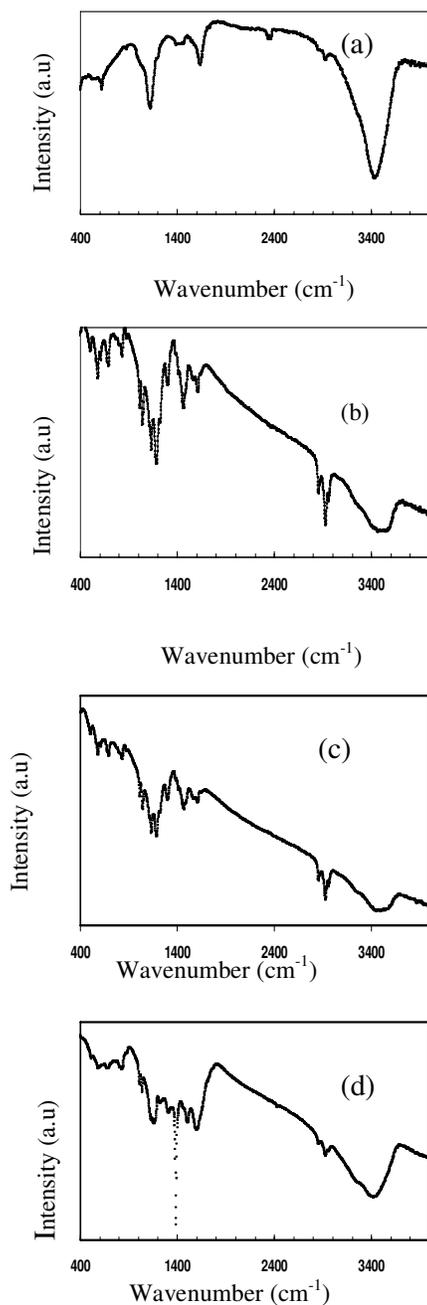


Figure 1

The characteristic vibrational modes of MWCNT, C=C ($\sim 1650 \text{ cm}^{-1}$) and O-H ($\sim 3400 \text{ cm}^{-1}$) are apparent in spectrum (a). The C=C vibrations occur due to the internal defects and the O-H vibration is associated with the oxidation of the sample during sample purification. The high purity of CNTs is also important in CNT-composite preparation. The spectrum for the PANI (b) consists of major peaks centered at around 3500, 1579, 1473 and 1309 cm^{-1} which are typical of PANI. The spectrum shows quinoid band at 1579 cm^{-1} and benzene ring band at 1473 cm^{-1} . The spectrum also displays a small band at 1309 cm^{-1} which is associated imine group. The band of deprotonated PANI is visible at 1189 cm^{-1} and out of plane bending of benzene ring appears at 835 cm^{-1} . The N-H stretching band at 3500 and the C-H stretch band at 2854, 2929, 2960 cm^{-1} respectively are correctly observed in the spectrum. The spectrum of CNT after dispersion in PANI (figure 1c) with out nickel did not exhibit any major change from PANI spectrum. This shows no interaction between CNT and PANI. However, PANI/CNT doped with nickel shows few changes in the spectrum (figure 1d). The benzene ring band was found to be shifted to 1509 cm^{-1} . This is expected due to the interaction PANI with CNT. The major shift is observed for NH peak of PANI (3500 cm^{-1}), which is shifted to lower wavenumber (3426 cm^{-1}). The most interesting feature is the appearance of an additional band at 1400 cm^{-1} which is attributed to the nickel related peak. We confirmed the position of this peak by doping of CNT alone with nickel (figure 2).

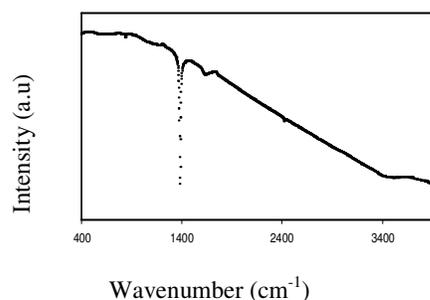


Figure 2

The presence of nickel in PANI/MWCNT/Ni composite is further confirmed by EDS analysis (figure 3). The schematic of the possible interaction is shown in figure 4. The SEM image of the PANI/MWCNT/Ni composite is shown in figure 5.

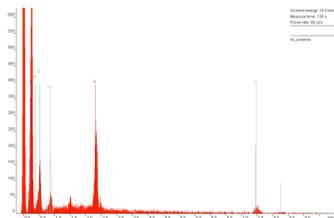


Figure 3

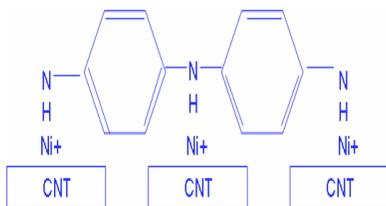


Figure 4

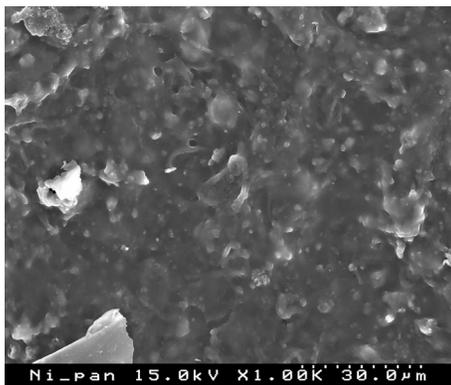


Figure 5

CONCLUSION

We assume nickel plays as an intermediate role in forming the composite. The interaction between PANI and CNT after nickel doping is confirmed by the shift in IR signal of NH vibrations. However, the exact role of nickel in forming uniform suspension of PANI/MWCNT has to be studied further. We propose this material for hydrogen storage due to the successful incorporation of nickel and CNT onto polymer matrix.

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