

Hydrogen Storage in Palladium Decorated Carbon Nanotubes Prepared by Solventless Method

R. Ravindra and Badekai Ramachandra Bhat

Abstract—Mass production of carbon nanotubes (CNTs) on an easy soluble support has been achieved by chemical vapor deposition method. CNTs have been synthesized using nickel formate as catalyst precursor at 700°C. The structure of the grown product was characterized by scanning electron microscopy, transmission electron microscopy, Raman spectroscopy and X-ray diffraction method. The purity of as grown product and purified product was determined by thermal analysis. The yield of CNTs was up to 8300 wt% relative to the catalyst have been achieved in the growth time of 15 mins. The purified product was decorated by palladium nanoparticles by solventless method. The palladium decorated CNTs were characterized by scanning electron microscope and X-ray diffraction method. The advantages of these routes are the simplicity and use of easily available low cost precursors. The hydrogenation behaviour of purified and decorated carbon nanotubes was carried out at room temperature and 90 bar pressure, using a high pressure Sieverts apparatus.

Index Terms—Carbon nanotubes, chemical vapor deposition, hydrogen storage, solventless method.

I. INTRODUCTION

Since the discovery in 1991 [1], carbon nanotubes (CNTs) have attracted much attention due to their outstanding mechanical and electronic properties. CNTs are potential candidates for many applications such as field emission devices [2], bio sensors [3], chemical sensors [4], hydrogen storage [5], nanoelectronics [6], catalyst support [7] and in composites as mechanical reinforcing agents [8]. Among the variety of synthesis techniques for CNTs, chemical vapor deposition (CVD) is the most suitable method for large scale production because of its low deposition, low cost and scalability. Composites composed of both metal nanoparticles and CNTs, in which nanoparticles are attached on the surface of the CNTs, have potential application in hydrogen storage, sensors, photo voltaics, heterogeneous catalysis and in electrocatalysis [9-10]. In this paper, we propose a novel approach to grow CNTs at high yield over nickel formate on easy soluble support using CVD method. This synthetic route is even more efficient than commercial ones employing metal oxide or nitrate as catalyst. The main advantage of use of nickel formate as catalyst precursor is that it avoids the lengthy process of reduction and calcination.

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By using calcium carbonate as support, problems such as detrimental effect, environment and even cost has been overcome. This technique leads to bulk production of CNTs in an economical way. Here we report 8300 wt% yield of CNTs synthesized over nickel formate.

We also propose to decorate grown CNTs by palladium nanoparticles by solventless method using palladium acetate as precursor. It was found that the size of the palladium nanoparticles on CNTs ranged from 10 to 20 nm. The main advantages of this synthetic strategy are simplicity, rapid, solventless and can be applied for bulk quantity of CNTs. In addition, hydrogen adsorption studies of purified and palladium decorated CNTs have been carried out and are discussed.

II. EXPERIMENTAL

A. Synthesis of CNTs

All reagents used were AR-grade and purchased from Sigma Aldrich. Nickel formate were prepared by nickel acetate and formic acid at 80°C. The microcrystalline precipitate was obtained on cooling which was filtered, dried at 100°C. The formation of nickel formate was confirmed by XRD. The supported catalyst was made by dispersing the nickel formate catalyst precursor on CaCO₃ powder. The CNTs were grown using the CVD technique (Fig. 1). Support with precursor weighing 0.3g was loaded into quartz boat. Thermolysis of the catalyst precursor develops nickel nanoparticles when boat is introduced into preheated tube in an argon atmosphere. On introduction of the acetylene gas, the growth of CNTs occurred. The CVD reaction was performed by passing a mixture of C₂H₂ 20 sccm:Ar 200 sccm for 15 mins at 700°C. The black product was collected after the reaction was cooled to room temperature in an argon atmosphere. To purify the sample, the raw material was first heated under an air atmosphere at 400°C for 2 hrs to ensure complete removal of amorphous carbon and then stirred in dilute HCl to remove the catalyst and support. The sample was finally washed with deionized water and dried in oven. The carbon yields were calculated by equation:

$$\frac{M_{Total} - M_{cat}}{M_{cat}} \times 100 = \text{carbon yield}\%$$

where M_{Total} is the total mass of carbon product and catalyst, and M_{cat} is the mass of catalyst

B. Decoration of CNTs by Palladium nanoparticles

CNTs were dry mixed with palladium acetate (10 wt%) using a mortar and pestle until homogeneous under ambient conditions. The solid mixture was then transferred to a quartz boat and heated in an argon atmosphere 350 °C for 2 h. The

product was then collected as the final Pd nanoparticle-decorated CNT nanohybrid sample.

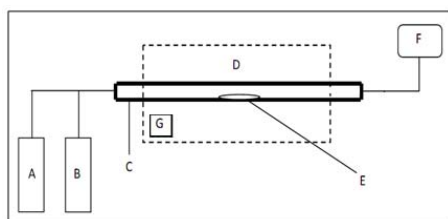


Fig. 1. Schematic representation of CVD set-up A-Argon gas cylinder B-Acetylene gas cylinder C-Quartz tube D-Furnace E- Quartz Boat F- Water bubbler G-Controller.

C. Characterization of CNTs and Decorated CNTs

The nanostructure and morphology of CNTs and decorated CNTs were observed under both scanning electron microscope (SEM, SUPRA 40VP Carl Zeiss) and transmission electron microscope (TEM, CM200, Philips). Thermal gravimetry analysis (TGA) was used to determine the purity and structural stabilities of CNTs. The TGA was performed on SDT Q600 (TA, USA) using dry air as the carrier gas (flow rate: 50 mL/min). The heating rate was 10°C/min. A Raman spectrum was obtained (Renishaw, RM 1000, He-Ne laser excitation line at 633.0 nm) to understand the relative intensity of G-band and D-band at ambient condition. The X-ray diffraction (XRD) patterns were obtained (JEOL JDX 8P diffractometer with Cu K α radiation, $\lambda=1.5418\text{\AA}$) to determine the crystallinity and purity of CNTs.

D. Hydrogen Adsorption Measurements

The hydrogen adsorption studies of the purified and palladium decorated carbon nanotubes were carried out using a high-pressure Sieverts apparatus, in the pressure of 90 bar and at room temperature. Before exposing to hydrogen, the carbon nanotubes were activated by heating up to a temperature of 175°C under a vacuum of 10^{-3} Torr for 2 h. Hydrogen was allowed at 100°C and then cooled to room temperature. The pressure-composition relationships were obtained by calculating the hydrogen storage capacity in wt% from the pressure drop during the hydrogen adsorption at constant temperature. After each cycle, the sample was degassed for 2 h at 175°C under a vacuum of 10^{-3} Torr.

III. RESULTS AND DISCUSSION

A. Synthesis of CNTs

Nickel formate precursor decompose directly into catalyst nickel nanoparticles without forming the oxide intermediate in a gas flow system. Thus this method of synthesizing metal nanoparticles as catalyst for the growth of carbon nanotubes has advantages over other inorganic salts like metal nitrates or oxides and even the lengthy process of calcination and reduction is eliminated. The support used for catalysts is CaCO₃, which is easily soluble in acid. So the problems such as detrimental effect on CNTs, environment and even cost has been overcome by using easy soluble substrate. The SEM and TEM morphology of purified CNTs are straight; however some helical and twisted ones are also present. The

diameter distribution is in the range 30-60 nm (Fig. 2a and 2b).

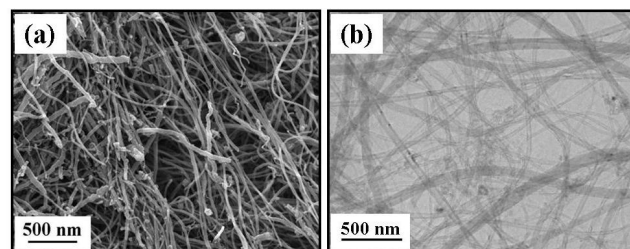


Fig. 2. (a) SEM and (b) TEM of purified carbon nanotubes.

Thermogravimetric analysis is a useful technique to estimate the purity of CNTs. The weight loss profile in Fig. 3 was obtained by heating the as grown and purified CNTs from room temperature to 700°C at a rate of 10°C/min in air atmosphere. The TGA curves indicate a significant mass drop around 500°C, which corresponds to the weight loss in the combustion of CNTs. The TGA graph also shows the evidence for the formation of very less amount of amorphous carbon. The quantitative analysis revealed that after the single-step purification, the purity of CNTs product was up to 99 %.

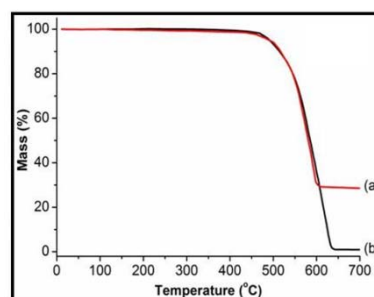


Fig. 3. TGA of (a) as grown and (b) purified carbon nanotubes.

Fig. 4 shows the powder XRD pattern of the purified CNT sample. The high and low peaks at 26.0° and 43.5° can be indexed to (002) and (101) diffraction planes of hexagonal graphite (JCPDS card files, no. 41-1487), respectively. The patterns clearly show that the CNTs are well graphitized and free from catalyst and support. Fig. 5 shows the Raman spectra of the purified CNTs. The spectra of all samples shows two broad bands at around 1329 cm⁻¹ (D-band) and 1586 cm⁻¹ (G-band) for purified CNTs. The G-band represents the degree of crystallinity in the graphite structure, while the D-band indicates the defects or impurities in the CNTs. The relative intensity ratio of D-band to G-band is known as an index for the crystalline order of CNTs. It was noted that I_D/I_G ratio of purified CNTs is more than unity, indicates that defect level in the CNTs is high.

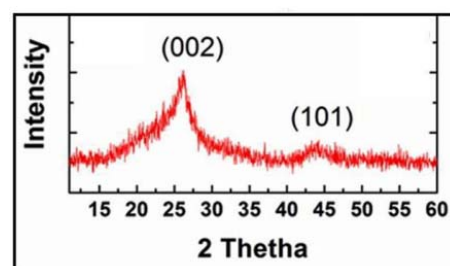


Fig. 4. XRD of purified carbon nanotubes.

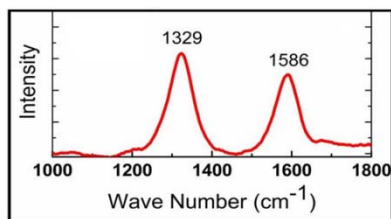


Fig. 5. Raman spectra of purified carbon nanotubes.

B. Decoration of CNTs by Palladium Nanoparticles

The XRD pattern of Pd-CNTs is shown in Fig. 6a. The major diffraction of Pd nanoparticles are observed. The reflections at $2\theta=40.2, 46.7$ and 68.3° correspond to the (111), (200) and (220) planes of a face centered cubic lattice of Pd nanoparticles, respectively (JCPDS card files, no. 87-0639). SEM images that show the morphologies of the Pd particles on the CNTs are shown in Fig. 6b. The homogeneous of uniform dark spots observable in the figure corresponds to Pd particles that are highly dispersed on the CNTs. The average sizes of the Pd particles are from 10 to 30 nm. The simplicity, rapid, solventless and can be applied for bulk quantity of CNTs are the main advantages of this method.

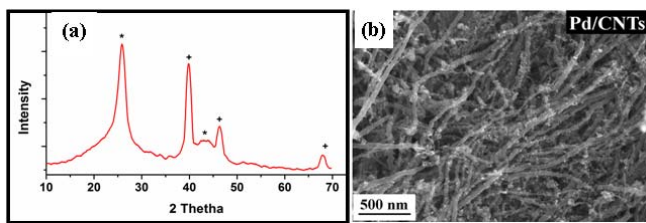


Fig. 6. (a) XRD and (b) SEM image of palladium decorated carbon nanotubes.

C. Hydrogen Storage Measurements

Hydrogen adsorptions were measured at 300K at hydrogen pressure range 20–90 bar for the purified carbon nanotubes. 5g of CNTs was loaded into sample holder; the sample was evacuated to 10^{-3} Torr and activated with flushing with H₂ for 2-3 times. The maximum hydrogen adsorption achieved for carbon nanotubes is 3.71 wt%. The adsorption increased as applied pressure increases. The 0.43, 2.05 and 3.71 wt % hydrogen adsorption was achieved at 20, 50 and 90 bar respectively as shown in the fig. 7-10. The hydrogen molecules could be physically adsorbed on the external nanotube walls and may be penetrated inside tubes (Fig. 11).

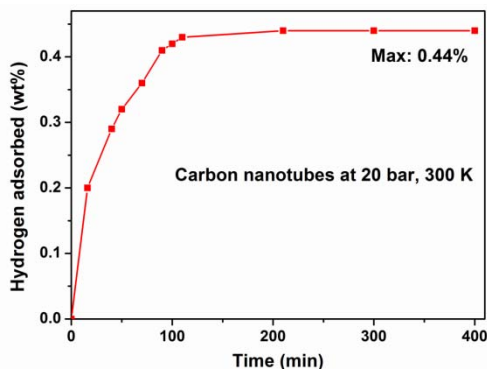


Fig. 7. Absorption kinetics of carbon nanotubes at 300K and 20 bar pressure.

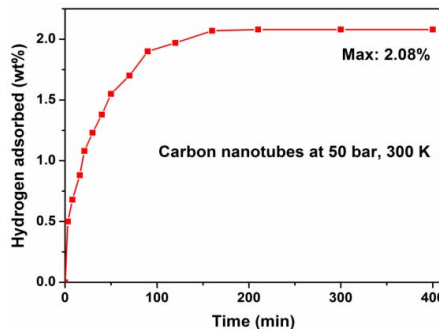


Fig. 8. Absorption kinetics of carbon nanotubes at 300K and 50 bar pressure.

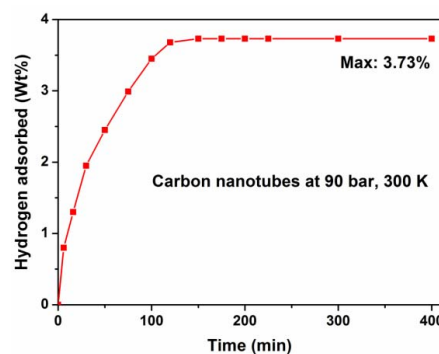


Fig. 9. Absorption kinetics of carbon nanotubes at 300K and 90 bar pressure.

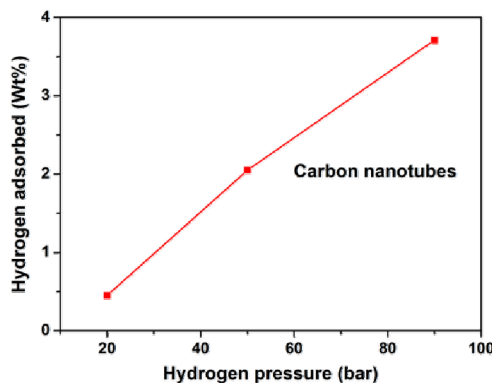


Fig. 10. Adsorption storage capacities of carbon nanofibers at different pressures.

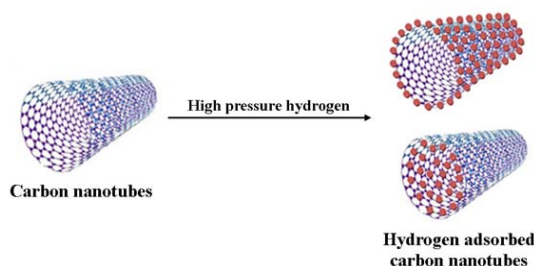


Fig. 11. Schematic representation of hydrogen adsorption in carbon nanotubes.

Hydrogen adsorptions were measured at 300K over the hydrogen pressure of 90 bar for palladium decorated carbon nanotubes. Around 5g of decorated CNTs were loaded into sample holder; the sample was evacuated to 10^{-3} Torr and activated with flushing with H₂ for 2-3 times. The maximum hydrogen storage achieved for palladium decorated CNTs is 3.98 wt% (Fig. 12).

The increase in hydrogen storage capacity in palladium decorated carbon nanotubes is due to 2 mechanisms;

1. Adsorption of the hydrogen molecules on the surface and interior regions of CNTs.

2. Dissociation of H₂ molecules on the palladium particles and atomic H spills over to the spaces between adjacent carbon layers of CNTs [11].

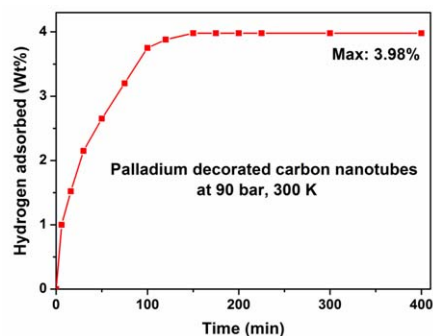


Fig. 12. Absorption kinetics of palladium decorated carbon nanotubes at 300K and 90 bar pressure.

IV. CONCLUSIONS

In this work, we have developed a simple method to synthesize CNTs in the bulk scale by CVD method. Nickel formate was used as catalyst because it forms nickel nanoparticles on pyrolysis. Calcium carbonate which is easily soluble in acid and non toxic is used as support. The yield of CNTs was up to 8300 wt% have been achieved in the growth time of 15 mins. The uses of acid and toxic materials are completely avoided. By this route we can grow CNTs in large scale by using low cost precursors in an economical and environmental friendly way. Palladium acetate was used as precursor to decorate CNTs by solventless method. The average sizes of the Pd particles on CNTs are from 10 to 30 nm. The simplicity, rapid, solventless and can be applied for bulk quantity of CNTs are the main advantages of this method. Hydrogen storage capacities of CNTs and palladium decorated CNTs were 3.73 and 3.98 wt%. The storage capacity increased as the applied hydrogen pressure increased for CNTs. The palladium decorated CNTs showed higher adsorption than CNTs due to higher binding energy between Pd and H atom.

REFERENCES

- [1] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, pp. 56-58, 1991.
- [2] H. J. Jeong, H. D. Jeong, H. Y. Kim, J. S. Kim, S. Y. Jeong, J. T. Han, D. S. Bang, and G. W. Lee, "All-Carbon Nanotube-Based Flexible Field-Emission Devices: From Cathode to Anode," *Adv. Funct. Mater.*, pp. 1526-1532, 2011.
- [3] X. Mao, Y. Wu, L. Xu, X. Cao, X. Cui, and L. Zhu, "Electrochemical biosensors based on redox carbon nanotubes prepared by noncovalent functionalization with 1, 10-phenanthroline-5, 6-dione," *Analyst*, vol. 136, pp. 293-298, 2011.
- [4] D. R. Kauffman and A. R. Star, "Graphene versus carbon nanotubes for chemical sensor and fuel cell applications," *Analyst*, vol. 135, pp. 2790-2797, 2010.
- [5] A. C. Dillon, K. M. Jones, T. A. Bekkedahl, C. H. Kiang, D. S. Bethune, and M. J. Heben, "Storage of hydrogen in single-walled carbon nanotubes," *Nature*, vol. 386, pp. 377-379, 1997.
- [6] B. Arne, "Nanoelectronics: Spin surprise in carbon," *Nature*, vol. 452, pp. 419-420, 2008.
- [7] D. Pan, J. Chen, W. Tao, L. Nie, and S. Yao, "Polyoxometalate-Modified Carbon Nanotubes: New Catalyst Support for Methanol Electro-oxidation," *Langmuir*, vol. 22, pp. 5872-5876, 2010.
- [8] Y. Wang, Z. Shi, and J. Yin, "Unzipped Multiwalled Carbon Nanotubes for Mechanical Reinforcement of Polymer Composites," *J. Phys. Chem. C*, vol. 114, pp. 19621-19628, 2010.
- [9] P. R. Somani, S. P. Somani, and M. Umeno, "Application of metal nanoparticles decorated carbon nanotubes in photovoltaics," *Appl. Phys. Lett.*, pp. 033315-033318, 2008.
- [10] C. Balazsi, "Novel hexagonal WO₃ nanopowder with metal decorated carbon nanotubes as NO₂ gas sensor," *Sens. Actuators A*, pp. 151-155, 2008.
- [11] A. Reyhani, S. Z. Mortazavi, S. Mirershadi, A. Z. Moshfegh, P. Parvin and A. N. Golikand, "Hydrogen Storage in Decorated Multiwalled Carbon Nanotubes by Ca, Co, Fe, Ni, and Pd Nanoparticles under Ambient Conditions," *J. Phy. Chem. C*, vol. 114, pp. 6994-7001, 2011.