

Increase of Hydrogen Storage Capacity of CNTs by Using Transition Metal, Metal Oxide–CNT Nanocomposites

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In this paper, we examined the synergetic effect of transition metals or their oxides as decorative agent with carbon nanotubes on the hydrogen storage capacity. The TiO₂, Pd, and PdO shell nanoparticles were used as decorative agent on the surface of carbon nanotubes. The samples were investigated by X-ray diffraction, Raman spectroscopy and transmission electron microscopy. The thermal stability was investigated by thermogravimetric analysis testing. The hydrogen storage capacity was measured by a custom-made Sieverts apparatus. The Pd and TiO₂ doped carbon nanotube shows the most marked hydrogen storage capacity, 7 times higher than pristine carbon nanotubes after 30 min storage. The results show that the hydrogen storage capacity of the PdO shell–carbon nanotube composite is very low in comparison with those of two others and does not represent a significant difference with that of carbon nanotubes.

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1. Introduction

Hydrogen is considered as future fuel due to its high energy density, ecological compatibility and reducing dependence to fossil fuels. For this reason, the storage of hydrogen safely and effectively is a very important challenge in its applications.

For the first time, Dillon et al. [1] claims a high hydrogen storage capacities in hollow cylinder of carbon nanotubes (CNTs) and their results show a possible 5–10 wt% hydrogen storage capacity for single walled carbon nanotubes (SWNTs). Subsequently, CNT was considered as a very promising candidate for hydrogen storage and great efforts were undertaken to investigate the hydrogen storage in CNTs [2]. Ye et al. [3] reported that a ratio of H to C atoms of about 1.0 was obtained for crystalline ropes of SWNTs at 80 K and pressures > 12 MPa. At a pressure of 4 MPa, a sudden increase in the adsorption capacities of the SWNT samples was reported, and they suspect that a structural phase transition is responsible for this effect.

However from the experimental results especially after 2003, serious doubt was arisen in relation to the high hydrogen storage capacities measured for carbon nanotubes and the results was not repeatable in various laboratories. In fact, by better purification of CNTs from the impurities like residual catalysts and other carbonaceous materials, the measured values of hydrogen storage of CNTs was considerably negligible [4]. For the first time, Hirscher and Becher [5] focused on the contradictory of the hydrogen storage results in CNTs. All of the newer results was in good agreement by the Hirscher claim and

reported very negligible values for purified carbon nanotubes and other *SP*² hybridized carbon morphologies [6, 7] which could not satisfy the goal of the USA department of energy (DOE) [8] asking for hydrogen storage capacity of 9.0 wt% by the FY 2015.

It is believed that modification of CNTs by decoration with transition and transition metal oxide nanoparticles provides the most proper method for practical use of CNTs in vehicles. Many studies have revealed that H₂ spill-over on the added particles is a promising approach to enhance the hydrogen storage in CNTs [9, 10]. These nanoparticles on CNTs are well-known for catalytical dissociation of hydrogen molecules on the CNT surface and activation of hydrogen adsorption sites. Active metallic nanoparticles such as Pt and Pd [9–14], and metal oxide nanoparticles especially MgO and TiO₂ [15–18] could considerably facilitate storage of hydrogen. In the case of transition metal oxides, metallic nanoparticles form active catalyst centers which trap hydrogen molecules in crystalline structure of metal oxides and decompose them into atoms.

In this work, we compare the effects of TiO₂, Pd and PdO nanoparticles used as decorative agent on the surface of carbon nanotubes in order to increase hydrogen storage capacity. Then the highest value of hydrogen storage will be compared to those reported in the literature at the same conditions.

2. Experimental methods

2.1. Materials and methods

Single walled carbon nanotubes (SWNT) prepared by chemical vapor deposition (CVD) method with specific surface area of 700 m²/g and diameter of 2 nm were purchased from Research Institute of Petroleum Industry (RIPI) (www.ripi.com) [19]. In the purpose of removing the amorphous carbonous materials from purchased material, thermal oxidation treatment has been performed

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in air at 400 °C for 60 min. The as-purified CNTs were used without further acid washing or catalyst extraction in order to prevent their structure modification [20, 21].

We performed H₂ adsorption experiments by using the as-purified SWNT and also with three treated samples from the same SWCNT batch. Three samples, each of 1000 mg in weight were pretreated in three different ways, and then were denoted as sample 1, sample 2 and sample 3.

Sample 1 was prepared by co-ultrasonication of TiO₂:CNT with weight ratio of 5 wt% in ethanol media at 60 °C until complete distillation of solvent. The anatase TiO₂ powder was purchased from EVONIC company with > 95% purity. Prior to co-ultrasonication of nanocomposite, each of precursors were stirred/sonicated in ethanol for 30 min independently [15]. In order to remove remaining solvent perfectly, nanocomposites were put into conventional oven at 100 °C for 60 min. Two other samples were prepared by dispersion and then reduction of Pd nanoparticles on CNTs surface using the method proposed by Wu et al. [10]. In this way, a mixture of SWNT and Pd acetylacetonate (Pd(C₅H₇O₂)₂) with 2 wt% Pd:SWNT ratio, was stirred at ambient temperature for 12 h. Solution was put into a vacuum oven at 60 °C for 12 h to remove solvent completely. In order to reduce Pd nanoparticles on the surface of CNTs, nanocomposites were placed under 100 sccm H₂ flow at 400 °C for 3 h. Sample 2 was prepared by a quick exiting of the sample from oven. The powder color was intensively turned dark red immediately after leaving out the oven. Sample 3 was prepared by cooling the same nanocomposite at ambient temperature under H₂ flow before leaving the oven.

2.2. Physical characterization

Thermogravimetric analysis (TGA) with a Rheometric Scientific SDA 1500 apparatus and the Raman spectroscopy analysis with the Jobin LabRam HR-800 Stokes mode with 532 nm frequency-doubled Nd:YAG laser excitation were used to evaluate thermal stability and quality of the CNTs, respectively. Transmission electron mi-

croscopy (TEM) images were obtained by using Philips EM208S TEM, 100 kV. The sample structure was determined by X-ray diffraction (XRD) analysis. XRD spectra were recorded in the range of $2\theta = 10^\circ$ and 90° with a step size of 0.05° using monochromatic Cu K_{α_1} radiation (XRD, PW1800, Philips). The elemental composition of the samples was characterized using a scanning electron microscope (Philips XL 30) equipped with a electron dispersive energy X-ray analysis system (EDX) which is unable to detect the elements lighter than Na.

2.3. Measurement of hydrogen adsorption

In this paper, we investigated hydrogen storage capacity of different samples by using custom-made Sieverts apparatus [4]. In this method, 0.8 g of each sample was placed in the reactor and then the measurements were carried out by first desorbing the hydrogen in the prepared samples at 200 °C for 1 h under vacuum (10^{-2} Pa). When the reactor (sample cell) was cooled down to room temperature, H₂ was introduced into the reactor to a certain pressure (about 30 atm), then the changes in pressure were monitored versus time. The accuracy of the the Sievert apparatus was measured by using a standard MgH₂ sample and was $\pm 10\%$.

3. Results and discussion

Figure 1 shows the TGA and Raman spectroscopy of as-purified SWNT. The thermogravimetric measurements show that the content of the catalyst residue in the SWNT is about 5 wt% and the amount of amorphous carbon at 550 °C is about 15 wt%, so the purity of our SWNT may be in the range of 70 to 80 wt%. The existence of SWNT can be proved by a peak in the radial breathing modes (RBM) region (between 200 and 300 cm⁻¹, which is representative of the isotropic radial expansion of the tube) of the Raman spectrum (inner plot of Fig. 1b). The diameter of the SWNT is given by $f = 234/D$, where f is the RBM frequency in cm⁻¹ and D is the nanotube diameter in nm. Thus, we obtain an average diameter of 2 nm for the nanotubes which is consistent with the seller claim.

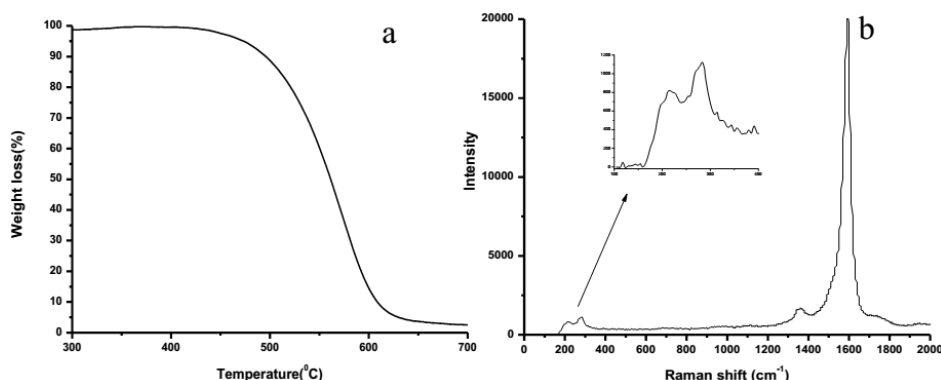


Fig. 1. (a) TGA and (b) Raman spectrum of as-purified SWNT.

Two other peaks displayed in Fig. 1b at about 1340 cm⁻¹ and 1580 cm⁻¹ are observed which are as-

signed to the *D* and *G* peaks of the CNTs. The lack of a broad peak between *D* and *G* bands could indicate

that there is a very low amount of amorphous carbon in as-purified sample (confirmed previously by thermogravimetric analysis (TGA)).

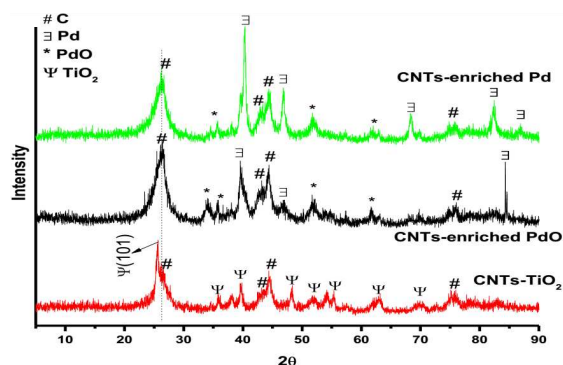


Fig. 2. XRD patterns of the nanocomposites.

X-ray diffraction patterns of all nanocomposites (samples 1, 2, and 3) exhibit the peaks of carbon corresponding to the SWCNT (Fig. 2). The presence of anatase

TiO₂ nanoparticles in sample 1 is confirmed by X-ray diffraction (XRD) pattern (JCPDS PD file No. 34-0180, 21-1276, and 21-1272 standard card). From the lower intensity of Pd in sample 2 at 40.3 degree in compare to sample 3 and also the greater intensity of PdO in sample 2 in comparison to sample 3 at 34 and 36 degrees, we can conclude that a great portion of sample 2 is oxidized. High percentage of Pd-SWNT nanocomposite is oxidized by a quick exit of the sample from oven because of high activity of Pd nanoparticles at 400 °C. This could be confirmed by the fact that the powder color were intensively turned dark red. This result shows the importance of cooling down stage of Pd-SWNT nanocomposite preparation and also the considerable oxidation tendency for doped Pd nanoparticles on the surface of CNTs at high temperatures. Moreover, Pd signals in sample 2 due to uncompleted oxidation of some Pd nanoparticles can probably be related to the formation of the shell/core structure of PdO/Pd nanoparticles. In the following we denote sample 2 and 3 by enriched PdO and enriched Pd, respectively.

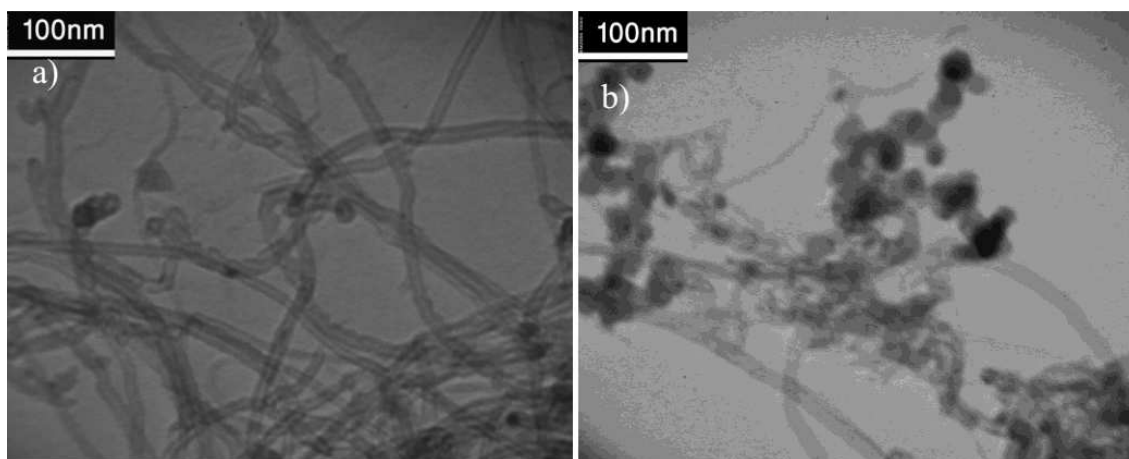


Fig. 3. TEM images of (a) as-purified CNTs and treated samples, (b) 1, (c) 2, and (d) 3.

Figure 3 shows TEM micrographs of as-purified and treated SWNT. One can clearly see a number of nanoparticles adhering to the CNT wall. An average size of 30 nm is estimated for the impregnated particles using TEM images.

Table shows the atomic concentration of the different dopant in nanocomposites obtained by EDX analysis. From the data, it can be inferred that the process used for TiO₂ nanoparticle dispersion is more effective than that of two others due to its higher atomic concentration.

Figure 4 shows the results for the H₂ adsorption in wt% for the four samples that are measured under an initial pressure about 30 atm at room temperature. The H₂ storage capacities for the four samples, from the lowest capacity to highest, are as-purified CNTs < sample 2 < sample 3 < sample 1. Sample 2 is highly oxidized in comparison to sample 3. The reduction of H₂ storage ca-

capacity in sample 2 in comparison to sample 3 is probably due to formation of a thick PdO layer which suppresses the activity of Pd catalysis for hydrogen molecule dissociation.

Hydrogen storage capacity of different samples at stable state are summarized in Table. Results show that hydrogen adsorption of the titania and Pd impregnated nanocomposites enhances the hydrogen uptake of SWNT up to 7 times, indicating the effectiveness of these nanoparticles in improving the hydrogen storage capacity, even if the amount of hydrogen storage in our case is not significant for practical applications.

Wu et al. [10] have reported that hydrogen adsorption capacity of Pd doped double-walled carbon nanotubes (2 wt%) could repeatably achieve 3.5 wt%. Unfortunately, this result was not confirmed by others. For example in Ref. [14], hydrogen adsorption capacity of

TABLE

Hydrogen storage capacity and dopant concentration of different samples.

	Composition	Hydrogen storage [wt%]	[at.%]
SWNT		0.06	–
sample 1	TiO ₂ decorated SWNT	0.45	Ti(50)
sample 2	enriched PdO–SWNT	0.12	Pd(24)
sample 3	enriched Pd–SWNT	0.40	Pd(25)

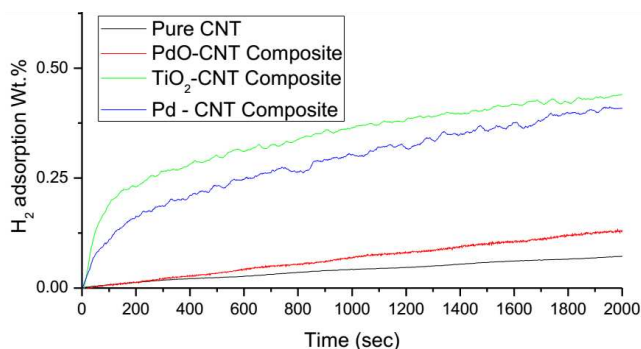


Fig. 4. Hydrogen adsorption of the samples versus adsorption time.

Pd doped multiwalled carbon nanotubes (MWCNTs) is reported to be 0.40 wt% which is in good agreement with our value. Rather et al. [16] have also reported a hydrogen storage of 0.40 wt% in nanostructured TiO₂-impregnated carbon nanotubes.

Bavykin et al. [19] have shown that anatase TiO₂ structure has a very convenient cavity for electrical adsorption of hydrogen atoms. The strong interactions between asymmetrically positioned Ti atoms in anatase (101) surface with hydrogen molecules can lead to hydrogen uptake.

Slight increase in hydrogen uptake by TiO₂ in comparison with Pd is due to the higher concentration of this one in the composite as revealed by EDX analysis (Table). Further study is ongoing to improve the dispersion process for Pd in order to obtain higher Pd concentration in the nanocomposite. We believe that higher Pd particle concentration can induce greater hydrogen storage capacity.

4. Conclusion

In this work, the hydrogen storage capacity of nanostructured anatase TiO₂, enriched Pd and PdO-carbon nanotube composite materials, performed at room temperature and moderate hydrogen pressure of 30 atm is presented. The hydrogen storage capacity of SWNT–TiO₂ and SWCNT-enriched Pd nanoparticles is 0.45 and 0.40 wt% respectively, which exhibit 7 times the storage capacity of pristine CNTs. Even if the measured values are far from practical hydrogen storage, it is noteworthy to consider their effectiveness in improving the hydrogen uptake. The SWCNT-enriched PdO nanocomposites

present a low capacity of hydrogen storage due to oxide layer which prohibits the activities of Pd nanoparticles for dissociation of hydrogen molecule.

Acknowledgments

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References

- [1] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, *Nature* **386**, 377 (1997).
- [2] R.G. Ding, G.Q. Lu, Z.F. Yan, M.A. Wilson, *J. Nanosci. Nanotechnol.* **1**, 7 (2001).
- [3] Y. Ye, C.C. Ahn, C. Witham, B. Fultz, J. Liu, A.G. Rinzler, D. Colbert, K.A. Smith, R.E. Smalley, *Appl. Phys. Lett.* **74**, 2307 (1999).
- [4] S. Safa, M. Mojtahedzadeh, V. Fatollahy, O.R. Kakuee, *Nano* **5**, 341 (2010).
- [5] M. Hirscher, M. Becher, *J. Nanosci. Nanotechnol.* **3**, 1 (2003).
- [6] W.C. Xu, K. Takahashi, Y. Matsuo, Y. Hattori, M. Kumagai, S. Ishiyama, K. Kaneko, S. Iijima, *Int. J. Hyd. Energy* **32**, 2504 (2007).
- [7] M. Hirscher, M. Becher, M. Haluska, A. Quintel, V. Skakalova, Y.-M. Choi, U. Dettlaff-Weglikowska, S. Roth, I. Stepanek, P. Bernier, A. Leonhardt, J. Fink, *J. Alloys Comp.* **330**, 654 (2002).
- [8] *DOE Hydrogen Program*, Annual Program Report, Department of Energy, 2006, p. 273.
- [9] S.B. Mishra, S.K. Mohapatra, O.A. Graeve, M. Misra, *Nanotechnology* **19**, 445607 (2008).
- [10] H. Wu, D. Wexler, A.R. Ranjbari, H. Liu, G. Wang, *Int. J. Hyd. Energy* **35**, 6345 (2010).
- [11] C.H. Chen, C.C. Huang, *Micropor. Mesopor. Mater.* **109**, 549 (2008).
- [12] R. Zacharia, S.U. Rather, S.W. Hwang, K.S. Nahm, *Chem. Phys. Lett.* **434**, 286 (2007).
- [13] J. Ozaki, W. Ohizumi, A. Oya, M.J. Illan-Gomez, M.C. Roman-Martinez, A. Linares-Solano, *Carbon* **38**, 778 (2000).
- [14] H.S. Kim, H. Lee, K.S. Han, J.H. Kim, M.S. Song, M.S. Park, *J. Phys. Chem. B* **109**, 8983 (2005).
- [15] Y. Suttisawat, P. Rangsunvigit, B. Kitiyanan, M. Williams, P. Ndungu, M.V. Lototsky, *Int. J. Hyd. Energy* **34**, 6669 (2009).
- [16] S.U. Rather, M. Naik, R. Zacharia, S.W. Hwang, R. Kim, K.S. Nahm, *Int. J. Hyd. Energy* **34**, 961 (2009).
- [17] V.F. Kiselev, O.V. Krylov, *Adsorption and Catalysis on Transition Metals and Their Oxides*, Springer-Verlag, New York 1989.
- [18] A. Lueking, R.T. Yang, *J. Catal.* **206**, 165 (2002).
- [19] D.V. Bavykin, A.A. Lapkin, P.K. Plucinski, J.M. Friedrich, F.C. Walsh, *J. Phys. Chem. B* **41**, 19422 (2005).
- [20] A. Rashidi, A. Horri, B.A. Mohajeri, A. Saraie, S. Jozani, K.J. Nakhaeipour, Continuous process for producing carbon nanotubes, US patent 20080274277, A1, Mar. 20 (2007).
- [21] K. Shen, D.L. Tierney, T. Pietrab, *Phys. Rev. B* **68**, 165418 (2003).