Increasing the Hydrogen Storage Capacity of Single-Walled Carbon Nanotube (SWNT) Through Facile Impregnation by Tio$_2$, Zro$_2$, and Zno Nanocatalysts

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ARTICLE INFO

ABSTRACT

Various nanocomposites of the TiO$_2$, ZnO and ZrO$_2$ decorated single wall carbon nanotubes (SWNTs) were fabricated by facile and template free continuous ultrasonication/stirring of virgin metal oxide nanopowders and SWNTs in ethanol under UV-light illumination. The TEM micrographs showed that nanoparticles (NPs) were uniformly dispersed and bonded on the surface of SWNTs. The results of XRD as well as FTIR spectroscopy revealed coexistence of the precursors in each nanocomposite. Hydrogen storage capacity of the nanocomposites was evaluated by a purpose-built sievert-type apparatus in kinetic mode measurement. The reversible values of hydrogen storage of the virgin SWNTs as well as the nanocomposites TiO$_2$, ZrO$_2$ and ZnO decorated SWNTs at room temperature were obtained as 0.08, 0.4, 0.31 and 0.25 wt.%, respectively. The considerable absorption ability in decorated nanocomposites was explained by catalytical effect of metal oxides in dissociation and compression of hydrogen into the absorbent sites of CNTs.

1. Introduction

Hydrogen storage properties of different materials such as metal hydrides, metal organic frameworks, and carbon materials have been reported [1-4]. Among them, carbon materials have received special attention due to their low density and good recycling properties.

Carbon nanotubes (CNTs), because of their large theoretical surface area and narrow pore size distribution, Among carbon materials, CNTs have potential advantages for hydrogen adsorption. Dillon *et al.* [5] worked for first time on hydrogen storage capacity and reported a possible 5 – 10 wt.% hydrogen storage for single walled carbon nanotubes.

Nevertheless, the experimental data about H$_2$ storage in pristine CNTs are unfavorable [3-] and it is believed that modification of CNTs by decoration with active metal and/or metal oxide nanoparticles provides the most suitable method for elevating the hydrogen storage capacity and facilitating the practical use of CNTs in vehicles [7-10].

In the case of transition metal oxides,

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nanoparticles form active catalyst centers which trap the hydrogen molecules in the crystalline structure of metal oxide and decompose them to atoms [10]. For example, Pan *et al.* [11] proved that hydrogen can effectively bind to the surface of TiO_2 and thendecompose to atoms even at room temperature.

However, to our knowledge, none of these investigations have compared the catalytical effect of various nanoparticles on hydrogen storage behavior of SWNTs. In this work, ZrO_2, ZnO and TiO_2 nanoparticles are bonded on the surface of SWNTs using simple co-ultrasonication/stirring of precursors under high power UV-illumination, as previously reported by Rather *etal*. [12]. Then the hydrogen storage of nanocomposites was measured and compared using a purpose-built sievert type apparatus.

2. Experimental
2. 1. Materials and methods
Single walled carbon nanotubes with specific surface area of 700 m^2/g and diameter of 2 nm were purchased from Research Institute of Petroleum Industry (RIPI) (www.ripi.com) [13]. They have been synthesized by thermal chemical vapor deposition (TCVD) method and have a purity of more than 60 % in weight. The CNTs were used with further purification by air oxidation at 400 ^{o}C for 60 min to remove amorphous carbonaceous materials from SWNTs. The anatase TiO_2 with average grain size of 20 – 25 nm, the mixed monoclinic-tetragonal ZrO_2 with average grain size of 20 - 25 nm and wurtzite ZnO nanoparticles with average grain size of 15 - 20 nm were used as-purchased from Tecnon Company with > 98 % purity.

For preparation of nanocomposites, each of the precursors was separately ultrasonicated/stirred in ethanol for 30 min. The samples were prepared by co-ultrasonication of SWNTs:TiO_2, SWNTs:ZnO and SWNTs:ZrO_2 (with 10 wt.% of metal oxides) for 120 min and were denoted as samples 1 to 3, respectively. Afterwards, the suspensions were thoroughly stirred at 60 ^{o}C under 40 W/cm^2 UV-illumination to eliminate the remained

ethanol and make heterojunction between nanoparticles and SWNTs. In order to completelyremove the remained solvent, nanocomposites were put into a conventional oven at 100 ^{o}C for 60 min.

2. 2. Physical characterization
Thermogravimetric analysis (TGA) with a Rheometric Scientific SDA 1500 apparatus and Raman spectroscopy analysis with a 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 purified SWNTs, respectively. TEM images were obtained by using transmission electron microscopy (Philips EM208S-100 kV). The samples for TEM measurement were prepared by placing a droplet of the admixed solution on a copper grid. The crystal structure of the samples was determined by X-ray diffraction (XRD) analysis. XRD spectra were recorded in the range of $2\theta=10^o$ and 90° with the step size of 0.05^o using monochromatic Cu-Kα Radiation (XRD, PW1800, Philips). Fourier transform infrared spectra (FTIR) were recorded on a Nicolet spectrometer using KBr pellets in transmission mode. Hydrogen absorption was measured in a purpose-built sievert type apparatus. For the hydrogen uptake experiments 2 g of each sample was loaded in a cylindrical stainless-steel reactor and evacuated to 10^{-3} mbar for 30 min. After evacuating the system, the measurements were carried out under H_2 pressure of 20 bar. Each hydrogen absorption kinetic curve was plotted automatically for about 400 s corresponding to the time when it reaches equilibrium.

3. Results and Discussion
Fig. 1 shows the TGA and Raman spectroscopy of purified SWNTs. It is known that amorphous structure of carbon is less stable and weaker than C-C bonds [14] which would be dissociated in lower temperatures (about 450 ℃) compared to graphitized carbon nanotube allotrope (> 500 ℃). So, it is convenient to evaluate the purity of CNTs by determining the residual metallic impurities at temperatures above> 650 ℃ and amorphous carbonaceous
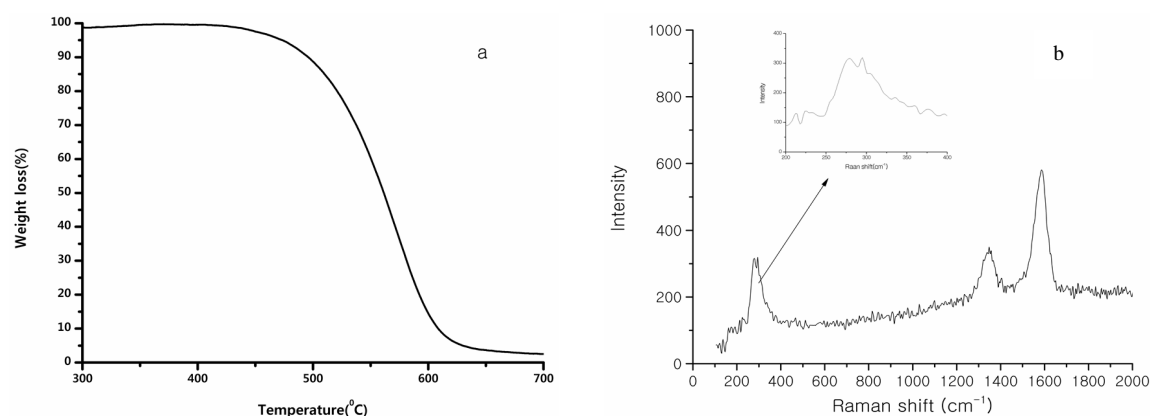
Fig. 1. a) TG curve obtained at 10 °C / min in air (20 ml/min) for purified CNTs and b) the corresponding Raman spectrum of purified CNTs (The inset presents radial breathing mode (RBM) of CNTs.)

allotropes by observed weigh loss at temperatures below 500 °C. Thus, thermogravimetric measurement showed that the content of the catalyst residue in the virgin SWNTs is lower than 5 wt% and the amount of amorphous carbon at 500 °C is ~12 wt%; so the purity of our SWNTs can be in the range of 80-85 wt. %.

A Raman spectrum of the SWCNTs contains three regions. One is low frequency region (between 200-400 cm^{-1}, RBM region), which is used to determine the diameter of SWCNTs. At high frequencies (about 1580cm^{-1}), the presence of graphitic line (G-line) is assigned to the Raman-allowed E_{2g} mode (the second region). At medium high frequencies (about 1340 cm^{-1}), the presence of the defect induced line (D-line) is assigned to A_{1g} phonon mode (the third region). The absence of a broad peak between D and G bands indicates that there is a low amount of amorphous carbon in purified sample (confirmed by TGA).

In addition, the Raman results show that SWNTs involve a considerable fraction of purified carbon nanotubes where the existence of SWNTs can be proved by a strong peak in the RBM region of Raman spectrum (inset plot of Fig. 1b). The diameter of SWNTs is estimated to be < 0.8 nm using the equation of $v = 223.75/d$ where v is RBM frequency in cm^{-1} and d is SWNT diameter in nm [3].

Fig. 2a-d shows TEM micrographs of the virgin and TiO$_2$, ZnO and ZrO$_2$ decorated SWNTs. It can be seen from the low and high magnified micrographs that numerous nanoparticles were appropriately adhered to the CNT wall, indicating that the facile ultrasonication/stirring is an appropriate method for composing nano-precursors. Moreover, it can be observed that nanoparticles with the size of < 50 nm are irregularly adhered to the outer body of CNTs in various points. Thus, one can conclude that the catalyst nanoparticles can appropriately adsorb, dissociate and compress the hydrogen molecules into the CNTs.

X-ray diffraction pattern of nanocomposites exhibit strong graphitic peaks corresponded to the SWNTs (Fig. 3). For example, two various peaks at 27.3 and 44.1° are diffracted from the C(001) and C(002) planes [15]. Also, the presence of various nanoparticles in each sample can be inferred from the XRD pattern.

A typical infrared (IR) spectrum of the virgin and TiO$_2$ impregnated SWNTs was recorded on a KBr background in transmission mode from 400 to 4000 cm^{-1}. The spectra were analyzed by correlating the absorption bands in the measured spectrum with the known absorption frequencies for different types of bonds.

In the high frequency region, broadened bands around 3420 cm^{-1} can be assigned to the bending vibration of the adsorbed molecular water and the stretching vibrations of OH groups. The peak at 2920 cm^{-1} corresponds to the C-H stretch vibration. The peaks at 1630 cm^{-1} can be inferred as CO stretching vibration in the both spectra [16].

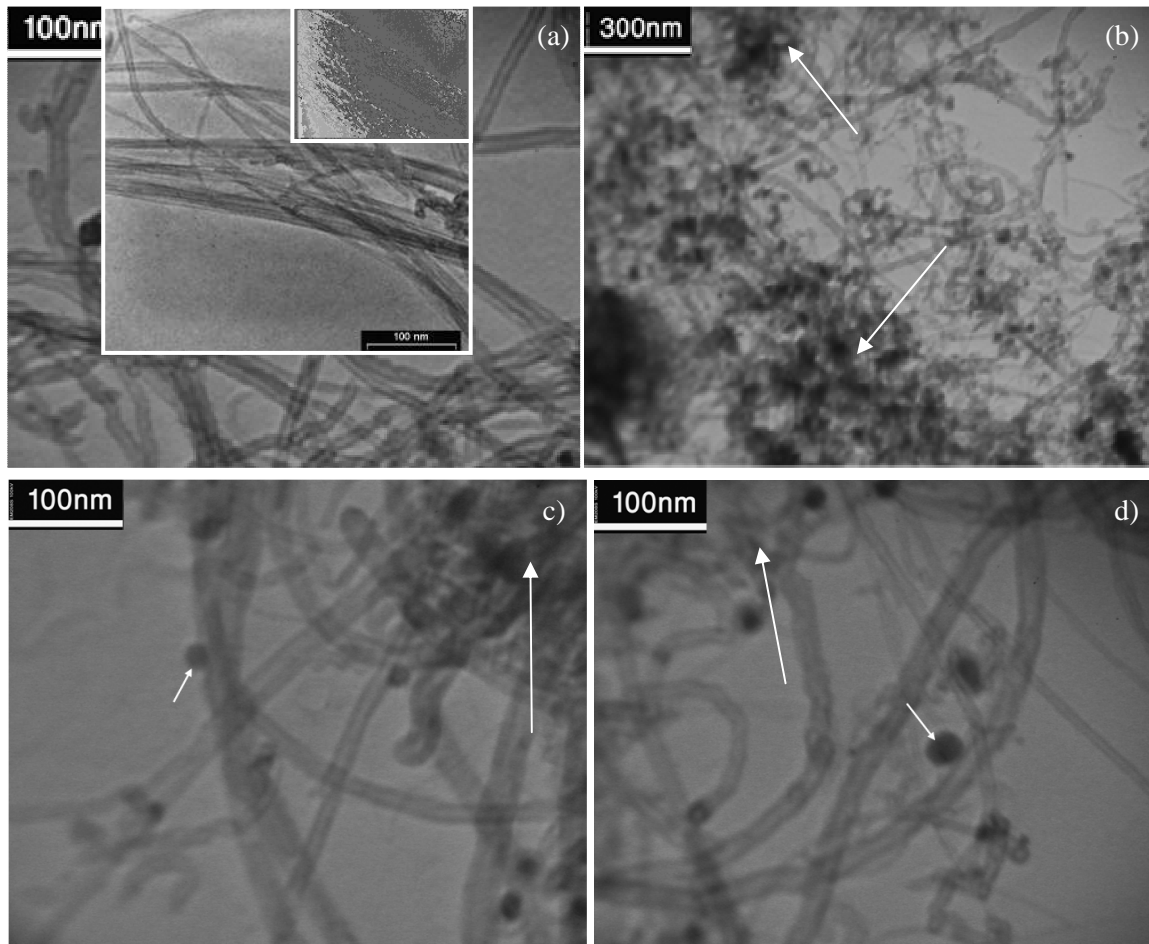The obtained IR spectra have several prominent bands in the region ranging 1033–1378cm-1 which is mostly attributed to

Fig. 2. TEM images of a) virgin CNTs and b) TiO_2, c) ZnO and d) ZrO_2 impregnated samples (For better comparison, the high-magnification TEM images of bare CNTs is observed in the inset of image a.)
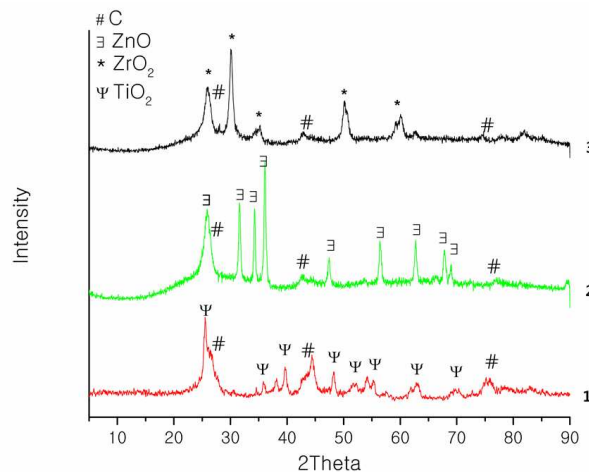

Fig. 3. XRD pattern of the samples 1-3

the aliphatic stretching frequencies of CH, CH_2 and CH_3 [17].

Compared with pure SWNTs (Fig. 4(b)), the peaks of the decorated sample (Fig.4 (a)) are a little weak. This suggests that the surface of SWNTs has probably been partially covered by TiO_2. Moreover, a significant shift to lower vibrational bands with respect to the pure
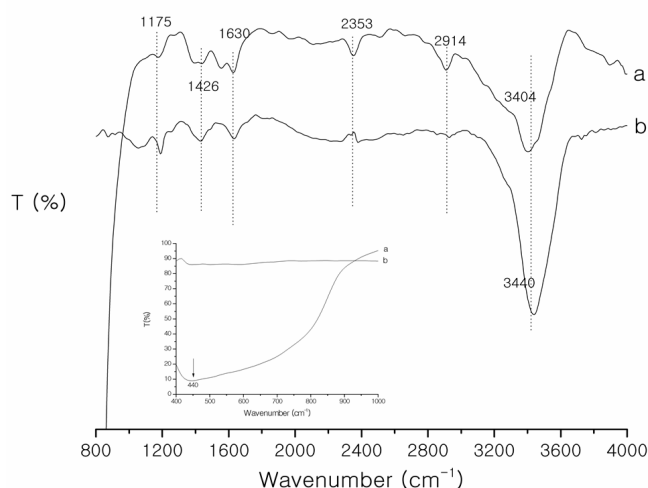
Fig. 4. FTIR spectra of a) TiO$_2$ impregnated SWNTs and b) virgin purified SWNTs (The inset presents lower frequencies mode of TiO$_2$ impregnated SWNTs.)
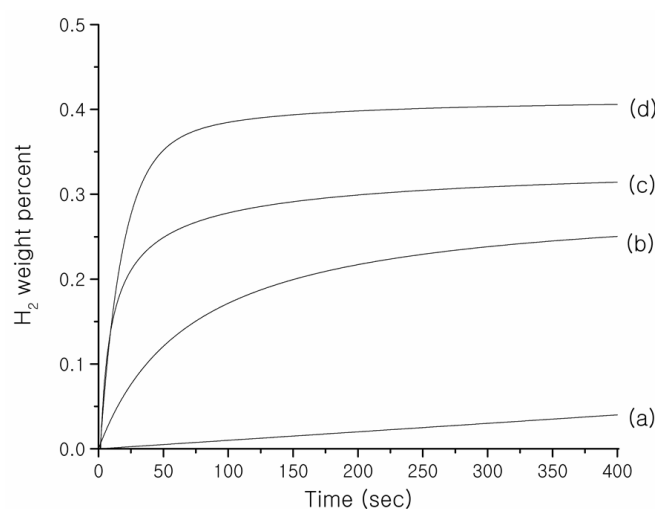

Fig. 5. Kinetic of hydrogen storage of a) raw SWNTs, b)ZnO-SWNTs, c) ZrO$_2$-SWNTs and d) TiO$_2$-SWNTs nanocomposite

SWNTs is attributed to the titania-SWNTs side wall bonding [16 ,18]. Furthermore, a broad peak at low vibrational bands (around 500 – 800 cm^{-1} in CNT/TiO$_2$ nanocomposite could be assigned to the combination effects of both Ti–O and Ti-O-C bands [16-19]. Akhavan *et al.* [20] suggested that UV illumination could dissociate the C-C bonds in carbonaceous allotropes and form new hetrojunctions such as Ti-O-C, by a photocatalytic interaction.

Fig. 5 presents the hydrogen absorption kinetic curve of purified SWNTs and the samples modified with different metal oxides at 300 K. It was found that the virgin SWNTs stored nearly 0.04 wt. %. Hydrogen storage capacity of the samples decorated by TiO$_2$, ZrO$_2$ and ZnO NPs significantly enhances to 0.4, 0.31 and 0.25 wt. %, respectively. It is suggested that the active metal oxides dissociate the hydrogen to atoms and then they can freely migrate and be stabilized on the surface and inside of SWNTs [10-12]. This is consistent with the results of other investigations and this phenomenon is called "hydrogen spillover" [10, 21-24].

Bavykin *et al.* [25] suggested that hydrogen atoms could electrically be absorbed into the holes of the oxide phase and then transmigrate to the CNTs. Thus, the difference in the size and type of holes affects the rate of hydrogen

compression into the CNTs. For this reason, from the observed rate and capacity of hydrogen, one could deduce that the most convenient hole for hydrogen is for TiO_2, ZrO_2 and ZnO, respectively.

Also, it can be noted from the figure that the initial hydrogen uptake rate has been substantially improved by metal oxides, especially TiO_2 and ZrO_2 NPs. By comparing the amount of stored hydrogen by each sample in the initial 100 s, one could see that pristine SWNTs have only adsorbed nearly 22 % of total capacity in 400 s, while the samples impregnated by TiO_2, ZrO_2 and ZnO have taken about 95, 88 and 64 wt.% of their total capacity.

4. Conclusions

We report a facile method for incorporation of various metal oxide nanoparticles on the SWNTs. The formation of Ti-O-C bonds in the FTIR spectra as well as the strong peaks of graphite in the XRD patterns suggest the formation of heterojunction between metal-oxides with CNTs. The low and high magnified TEM micrographs showed that nanoparticles were appropriately adhered on the CNTs walls. Hydrogen storage capacity of nanocomposites revealed a significant effect of nanocatalyst especially titania nanoparticles in dissociation and migration of H_2 into the SWNTs. Moreover, it was found that anatase titania shows the best activity for dissociation and compression the hydrogen into SWNTs.

Acknowledgements

References

1. J. J. Reilly, G. D. Sandrock. "Hydrogen storage in metal hydrides." Scientific American, vol. 242, 1980, pp. 118.

2. M. P. Suh, Hye Jeong Park, Thazhe Kootteri Prasad, Dae-Woon Lim. "Hydrogen storage in metal–organic frameworks." Chemical reviews, vol. 112, no. 2, 2011, pp. 782-835.

3. S. Safa, M. Mojtahedzadeh Larijani, V. Fathollahi, O. R. Kakuee. "Investigating hydrogen storage behavior of carbon nanotubes at ambient temperature and above by ion beam analysis." Nano, vol. 5, no. 06, 2010, pp. 341-347.

4. A. H. Noroozi, S. Safa, R. Azimirad, H. R. Shirzadi, N. G. Yazdi. "Microstructure and Hydrogen Storage Properties of LaNi5-Multi Wall Carbon Nanotubes (MWCNTs) Composite." Arabian Journal for Science and Engineering, vol. 38, no. 1, 2013, pp. 187-194.

5. A. C. Dillon, M. J. Heben. "Hydrogen storage using carbon adsorbents: past, present and future." Applied Physics A, vol. 72, 2001, pp. 133-142.

6. E. Mosquera, Donovan E. Diaz-Droguett, Nicolás Carvajal, Martin Roble, Mauricio Morel, Rodrigo Espinoza. "Characterization and hydrogen storage in multi-walled carbon nanotubes grown by aerosol-assisted CVD method." Diamond and Related Materials, vol. 43, 2014, pp. 66-71.

7. W. M. Daoush, T. Imae. "Syntheses and characterizations of multiwalled carbon nanotubes-supported palladium nanocomposites." Journal of Materials Research, vol. 27, no. 13, vol. 2012, pp. 1680-1687.

8. T. Yildirim, S. Ciraci. "Titanium-decorated carbon nanotubes as a potential high-capacity hydrogen storage medium." Physical review letters, vol. 94, no. 17, 2005, pp. 175501.

9. H. Imamura, Mitsuya Kusuhara, Shoko Minami, Masayoshi Matsumoto, Kazuo Masanari, Yoshihisa Sakata, Keiji Itoh, Toshiharu Fukunaga. "Carbon nanocomposites synthesized by high-energy mechanical milling of graphite and magnesium for hydrogen storage." Acta materialia, vol. 51, no. 20, 2003, pp. 6407-6414.

10. R. Zacharia, Sami-ullah Rather, Sang Woon Hwang, Kee Suk Nahm. "Spillover of physisorbed hydrogen from sputter-deposited arrays of platinum nanoparticles to multi-walled carbon nanotubes." Chemical physics letters, vol. 434, no. 4, 2007, pp. 286-291.

11. J. M. Pan, B. L. Maschhoff, U. Diebold, T.

E. Madey. "Interaction of water, oxygen, and hydrogen with TiO2 (110) surfaces having different defect densities." Journal of Vacuum Science & Technology A, vol. 10, no. 4, 1992, pp. 2470-2476.

12. S. U. Rather, Naik Mehraj-ud-din, Renju Zacharia, Sang Woon Hwang, Ae Rahn Kim, Kee Suk Nahm. "Hydrogen storage of nanostructured TiO< sub> 2</sub>-impregnated carbon nanotubes." international journal of hydrogen energy, vol. 34, no. 2, 2009, pp. 961-966.

13. A. Rashidi, A. Horri, B. A. Mohajeri, A. Saraie, S. Jozani K. J. Nakhaeipor, Continuous process for producing carbon nanotubes. US patent 20080274277.

14. C. M. Chen, M. Chen, F. C. Leu, S. Y. Hsu, S. C. Wang, S. C. Shi, Chia-Fu Chen, Purification of multi-walled carbon nanotubes by microwave digestion method, Diamond and related materials, vol. 13, no. 4, 2004, pp. 1182-1186.

15. O. Akhavan, R. Azimirad, S. Safa, M. M. Larijani. "Visible light photo-induced antibacterial activity of CNT–doped TiO2 thin films with various CNT contents." Journal of Materials Chemistry, vol. 20, no. 35, 2010, pp.7386-7392.

16. U. J. Kim, Clascidia A. Furtado, Xiaoming Liu, Gugang Chen, Peter C. Eklund. "Raman and IR spectroscopy of chemically processed single-walled carbon nanotubes." Journal of the American Chemical Society, vol. 127, no. 44, 2005, pp. 15437-15445.

17. K. A. Byrappa, S. Dayananda, C. P. Sajan, B. Basavalingu, M. B. Shayan, K. Soga, M. Yoshimura. "Hydrothermal preparation of ZnO: CNT and TiO2: CNT composites and their photocatalytic applications." Journal of Materials Science, vol. 43, no. 7, 2008, pp. 2348-2355.

18. J. Wu, Xiaoping Shen, Lei Jiang, Kun Wang, Kangmin Chen. "Solvothermal synthesis and characterization of sandwich-like graphene/ZnO nanocomposites." Applied Surface Science, vol. 256, no. 9, 2010, pp. 2826-2830.

19. Y. Abdi, Maryam Khalilian, and Ezatollah Arzi. "Enhancement in photo-induced hydrophilicity of TiO2/CNT nanostructures by applying voltage." Journal of Physics D: Applied Physics, vol. 44, no. 25, 2011, 255405.

20. O. Akhavan, "Graphene nanomesh by ZnO nanorod photocatalysts." Acs Nano, vol. 4, no. 7, 2010, pp. 4174-4180.

21. J. S. Im, Jumi Yun, Jae-Geun Kim, Young-Seak Lee. "Preparation and Applications of Activated Electrospun Nanofibers for Energy Storage Materials." Current Organic Chemistry, vol. 17, no. 13, 2013, pp. 1424-1433.

22. F. H. Yang, Anthony J. Lachawiec, and Ralph T. Yang. "Adsorption of spillover hydrogen atoms on single-wall carbon nanotubes." *The Journal of Physical Chemistry B* 110, no. 12, 2006, pp. 6236-6244.

23. Chen, Chien-Hung, Chen-Chia Huang. "Enhancement of hydrogen spillover onto carbon nanotubes with defect feature." Microporous and Mesoporous Materials, vol. 109, no. 1, 2008, pp. 549-559.

24. L. Wang, Ralph T. Yang. "Hydrogen storage on carbon-based adsorbents and storage at ambient temperature by hydrogen spillover." Catalysis Reviews: Science and Engineering, vol. 52, no. 4, 2010, pp. 411-461.

25. D. V. Bavykin, Alexei A. Lapkin, Pawel K. Plucinski, Jens M. Friedrich, and Frank C. Walsh. "Reversible storage of molecular hydrogen by sorption into multilayered TiO2 nanotubes." The Journal of Physical Chemistry B, vol. 109, no. 41, 2005, pp. 19422-19427.