Effects of Reducing Temperatures on the Hydrogen Storage Capacity of Double-Walled Carbon Nanotubes with Pd Loading

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The effects of different temperatures on the hydrogen sorption characteristics of double-walled carbon nanotubes (DWCNTs) with palladium loading have been investigated. When we use different temperatures, the particle sizes and specific surface areas of the samples are different, which affects the hydrogen storage capacity of the DWCNTs. In this work, the amount of hydrogen storage capacity was determined (by AMC Gas Reactor Controller) to be 1.70, 1.85, 2.00, and 1.93 wt% for pristine DWCNTs and for 2%Pd/DWCNTs-300 °C, 2%Pd/DWCNTs-400 °C, and 2%Pd/DWCNTs-500 °C, respectively. We found that the hydrogen storage capacity can be enhanced by loading with 2% Pd nanoparticles and selecting a suitable temperature. Furthermore, the sorption can be attributed to the chemical reaction between atomic hydrogen and the dangling bonds of the DWCNTs.

Keywords: Hydrogen Storage, Carbon Nanotubes, Spillover, Adsorption.

Hydrogen has been considered as an ideal energy medium for replacing fossil fuels to mitigate global environmental problems. For the utilization of hydrogen, hydrogen storage technology is necessary, in which light and environmentally friendly materials are required to store the hydrogen.¹ A challenge that we have to contend with, however, is how to transport the hydrogen safely and efficiently.² According to the US Department of Energy, as reported in http://www.energy.gov, a carbon hydrogen storage material needs to store 6.5% of its own weight in hydrogen to make fuel cells that are practical in cars.

In 1991, Iijima described for the first time the new form of carbon called carbon nanotubes (CNTs).³ CNTs are ideal for adsorption of gases due to their unique micro-porous structure. Because of its sustainable and environmentally friendly character, hydrogen storage on CNTs has been investigated both experimentally and theoretically by many researchers.⁴⁻¹⁰ An alternative way of increasing the hydrogen adsorption capacities of CNTs is loading them with a transition metal. It is well known that a minor amount (~2 wt%) of a transition metal or noble metal, such as Pd, Pt, or Ni, dispersed on a carbon material can dissociate hydrogen molecules into hydrogen atoms and spill them over onto the carbon surfaces.¹¹ Anson et al.¹² prepared palladium loaded CNTs for hydrogen sorption and found that absorption was more than one order of magnitude greater than the physical adsorption on the raw carbon materials. It was also reported that by controlling the temperature, the surface areas and structures of the samples could be modified. Fujiwara et al.¹³ reported that heat treatment doubled the surface area of single-walled CNTs (SWCNTs) for both N₂ and O₂ adsorption.

In this study, we have investigated the hydrogen adsorption properties of 2%Pd/double walled CNTs (DWCNTs), using H₂ as the reductant at different temperature. Our results show that the choice of a suitable reducing temperature has a significant effect on the hydrogen adsorption, with 400 °C performing the best among the temperatures investigated.

All chemicals were American Chemical Society standard (ACS) reagents and purchased from Sigma-Aldrich. The pristine DWCNT sample was purchased from Carbon Nanotechnologies Inc., USA (grade DW0923). For the 2%Pd/DWCNTs-H₂, in order to load Pd nanoparticles on DWCNTs, pristine DWCNTs were mixed in ethanol with Pd(C₂H₃O₂)₂, to achieve a nominal Pd content of 2 wt% in the final material. The mixing was followed by stirring...
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Fig. 1. X-ray diffraction patterns of (1) pristine DWCNTs; (2) 2%Pd/DWCNTs-300 °C; (3) 2%Pd/DWCNTs-400 °C; and (4) 2%Pd/DWCNTs-500 °C.

at room temperature for 12 h. After that, the mixture was dried at 60 °C in a vacuum oven overnight and then was reduced at 300 °C, 400 °C, and 500 °C, respectively, for 3 h under H2 gas flow (150 mL/min). The phase identity of the Pd loaded DWCNTs was characterized by X-ray diffraction (XRD), using a GBC MMA X-ray diffractometer with Cu Kα radiation. The morphologies and nanostructures were analyzed by transmission electron microscopy (TEM) and high resolution TEM (HRTEM) using a JEOL JEM 2011 TEM instrument. TEM specimens were prepared by making a suspension in ethanol followed by deposition onto a holey carbon-coated copper grid. The Brunauer–Emmett–Teller (BET) surface areas were measured with a Quanta Chrome Nova 1000 Gas Sorption Analyzer using instrument N2 as the adsorbate at 77 K.

The hydrogen adsorption behavior of the samples was evaluated at ambient pressure and room temperature by the Sieverts method, using an AMC Gas Reactor Controller (Advanced Materials Corporation). All samples were dried for almost 4 h at 50 °C and vacuum degassed at 147 °C overnight before the sorption experiments.

Figure 1 shows the X-ray diffraction patterns (1), (2), (3), and (4) for the pristine DWCNTs, 2%Pd/DWCNTs-300 °C, 2%Pd/DWCNTs-400 °C, and 2%Pd/DWCNTs-500 °C, respectively. As expected, two broad peaks at 2θ = 26.7° and 43.7° correspond to graphite (002) and (100). For the 2%Pd/DWCNTs-300 °C, 2%Pd/DWCNTs-400 °C, and 2%Pd/DWCNTs-500 °C, two additional peaks are observed, which can be indexed to the cubic phase of Pd as (111) and (200). The widths of the two additional peaks in Figure 1 indicate that under the experimental conditions, different temperatures lead to different Pd particle sizes and states. In Figure 1(2), rather wide and shallow peaks are observed in the XRD pattern, which can be attributed to poor crystallinity of the Pd nanoparticles due to low temperature (300 °C) synthesis. Furthermore, we also confirmed that the Pd loading on DWCNTs did not lead to any structural changes in the carbon nanotubes.

Figure 2 shows TEM bright field micrographs of the pristine DWCNTs (Fig. 2(a)), 2%Pd/DWCNTs-300 °C (Fig. 2(b)), 2%Pd/DWCNTs-400 °C (Fig. 2(c)), and 2%Pd/DWCNTs-500 °C (Fig. 2(d)), respectively. The dark nanoparticles are the Pd catalysts particles. The selected area electron diffractions (SAED) patterns of the samples show associated spotty ring patterns, as in the insets in Figures 2(c) and (d) for 2%Pd/DWCNTs-400 °C and 2%Pd/DWCNTs-500 °C, respectively. The bright spots in the insets correspond to the Pd(111) and (002) CNT reflections, which confirms the presence of nanocrystalline Pd. However, the SAED pattern for the 2%Pd/DWCNTs-300 °C sample did not show the spotty ring for Pd, implying poor crystallinity of the Pd nanoparticles, which is consistent with the results of XRD analysis. Comparison of Figures 2(b)–(d) indicates the effects of different reducing temperatures on the general morphology and particle size of Pd loading on the DWCNTs. For 2%Pd/DWCNTs-300 °C (Fig. 2(b)), the Pd particles have a particle size of about 50 nm, but in Figure 2(c) for the 2%Pd/DWCNTs-400 °C sample, the bright field images of this Pd loaded sample exhibit a wide range of Pd nanocrystalline particle sizes, from 50 nm to less than 5 nm, and they are distributed randomly throughout the DWCNTs. For 2%Pd/DWCNTs-500 °C (Fig. 2(d)), the Pd particle size is the smallest, and it exhibits a wide range from 3 nm to 30 nm. This result is consistent with the results of XRD analysis. From this result, we can see that using high temperature can lead to small Pd particles, while low temperature can lead to poor crystallinity of the Pd nanoparticles. Furthermore, we performed quantitative energy dispersive X-ray (EDX) analysis. For each sample, the content of Pd was equal to the nominal ratio.

The specific surface areas of the pristine DWCNTs, 2%Pd/DWCNTs-300 °C, 2%Pd/DWCNTs-400 °C, and 2%Pd/DWCNTs-500 °C were measured to be 197.8 m2/g, 201.2 m2/g, 209.1 m2/g, and 205.4 m2/g, respectively. We found that loading Pd on the pristine DWCNTs can effectively increase the BET surface area of the DWCNTs. Among all the samples, the surface area of 2%Pd/DWCNTs-400 °C was the highest. These results demonstrate that defect sites could be created in the vicinity of the metal particles by the H2 reduction procedure at high temperature, due to the possible gasification of carbon that is catalyzed by the metal.15 The surface area of the 2%Pd/DWCNTs-500 °C sample, however, was lower than that of the 2%Pd/DWCNTs-400 °C. It is suggested that
some of the defects created are recrystallized during the annealing process at high temperature. The specific surface area of the 2%Pd/DWCNTs-300 °C, however, is lower than that of the 2%Pd/DWCNTs-400 °C, which may be because the extent of carbon gasification, due to catalysis by the metal is not the same at 300 °C as at 400 °C. Therefore, the BET surface areas of the DWCNTs samples are in the order: 2%Pd/DWCNTs-400 °C > 2%Pd/DWCNTs-500 °C > 2%Pd/DWCNTs-300 °C > pristine DWCNTs.

The effects of loading Pd nanoparticles on the pristine DWCNTs and annealing at different temperatures on the hydrogen storage properties of the DWCNTs were examined by hydrogen adsorption measurements, where hydrogen was adsorbed at 30 atm and 25 °C for 180 min. Figure 3 shows the results on the H₂ adsorption capacities of the four samples. The amount of hydrogen storage was determined to be 1.70, 1.85, 2.00, and 1.93 wt% for pristine DWCNTs, 2%Pd/DWCNTs-300 °C, 2%Pd/DWCNTs-400 °C, and 2%Pd/DWCNTs-500 °C, respectively. In comparison with the pristine DWCNTs, it is remarkable that the hydrogen adsorption capacity of the 2 wt%Pd/DWCNTs has been significantly enhanced. The hydrogen adsorption capacities of all the samples are higher than in Ref. [17], but lower than in Ref. [18]. Furthermore, it should be noted that the larger the specific surface area, the higher the hydrogen storage capacity. This could be attributed to the great number of adsorption sites for hydrogen in a receptor with a high surface area and full contact between Pd and the hydrogen molecules.

The mechanisms of H₂ storage in DWCNTs and 2%Pd/DWCNTs were studied in our previous papers. For the 2 wt%Pd DWCNTs, hydrogen is transferred to the DWCNTs by a cooperative effect between the palladium
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and the carbon network. Such hydrogen transfer, the so-called spillover effect, has been already reported in other systems, such as Pt and Pd catalysts supported on activated carbon (CA) or graphite nanofibers (GNF).2,1 Such spillover effects are very likely to occur in the present material, in which dihydrogen is dissociated by the Pd particles and transferred to the carbon network, where it is chemically bound. The binding energy is stronger than for physisorption, and such hydrogen cannot be released at room temperature.

In comparison with the 2%Pd/DWCNTs-400 °C, for the 2%Pd/DWCNTs-300 °C and Pd/DWCNTs-500 °C, the same amount of H₂ should be dissociated by the Pd catalyst, but the decreased concentration of defect sites could not provide enough positions for H₂ adsorption. The H₂ storage capacities are in the order: 2%Pd/DWCNTs-400 °C > 2%Pd/DWCNTs-500 °C > 2%Pd/DWCNTs-300 °C > pristine DWCNTs, which is in the same order as the BET surface areas.

In this paper, 2%Pd was loaded on DWCNTs at different temperatures. We found that the different temperatures had particular effects on the Pd particle size and the specific surface areas of the samples, which can change the hydrogen sorption characteristics. The loading of Pd on the DWCNTs is believed to promote the dissociation of H₂ molecules into hydrogen atoms, which will spill over to the defect sites on the DWCNTs. Furthermore, it should be noted that the larger the specific surface area is, the higher hydrogen storage capacity is.

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